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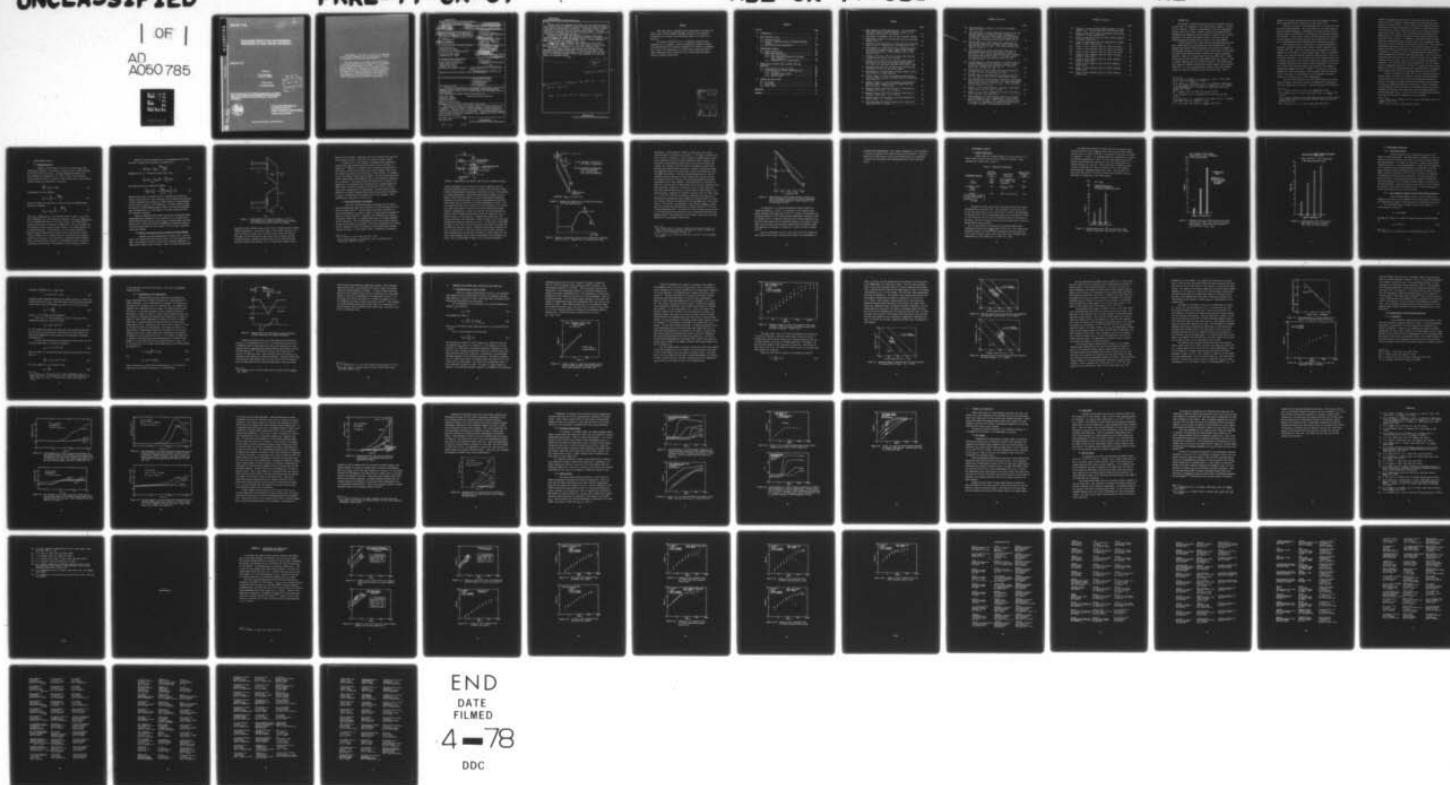
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HDL-CR-77-088, Radiation Effects on the Electrical Properties of MOS Device Materials,

by Gary W. Hughes

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## RADIATION EFFECTS ON THE ELECTRICAL PROPERTIES OF MOS DEVICE MATERIALS

FEBRUARY 1978

Prepared by

RCA Laboratories  
Princeton, NJ 08540

Under Contract

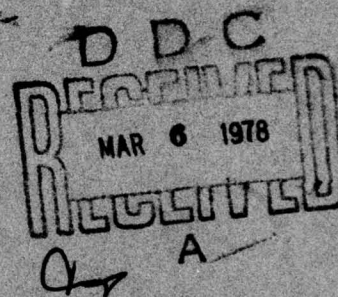
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Radiation-hard SiO <sub>2</sub> on Si grown by three different processes (dry, pyrogenic steam, and hybrid) has been examined by vacuum ultraviolet techniques. Flatband shift vs time measurements provide estimates of capture cross sections and trap densities. Current-enhancement measurements provide qualitative information about trapping at both the Si-SiO <sub>2</sub> and gate-SiO <sub>2</sub> interface.			

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Results show that unannealed dry oxides have the lowest interface-state density after irradiation, making them more desirable for applications where switching speed is important. Annealing in argon at 800°C increases both the hole-trap and interface-state density. All dry oxides have a dominant trap with capture cross section  $S \sim 5 \times 10^{-14} \text{ cm}^2$  at applied oxide fields  $E_0 = 1 \text{ MV/cm}$ .  $\epsilon_{\text{sub } 0}$

Pyrogenic steam oxides have many more interface states after irradiation than dry oxides and can be characterized by a dominant trap with  $S \sim 5 \times 10^{-14} - 10^{-13} \text{ cm}^2$  for  $E_0 = 1 \text{ MV/cm}$ . Oxides annealed at 900°C have the smallest density of hole traps.

Hybrid oxides grown in 3% HCl steam followed by dry O<sub>2</sub> show  $S \sim 2 \times 10^{-13} \text{ cm}^2$  at  $E_0 = 1 \text{ MV/cm}$ . The larger capture cross section for these oxides is believed to be due to the presence of HCl.

All oxides show a neutral trap capture cross section which is approximately inversely proportional to applied oxide field. Both pyrogenic steam and dry hard oxides can be characterized by the same trap. The difference between the two oxides appears to be only the density of interface states.

approx. =

$5 \times 10$  to the -14th power sq cm

\*  $5 \times 10$  to the -14th power to  $10$  to the -13th power sq. cm.

\*\*  $2 \times 10$  to the -13th power sq. cm

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## PREFACE

This final report, prepared by RCA Laboratories, Princeton, NJ 08540, under Contract DAAG39-76-C-0088, describes work performed principally in the Solid State Technology Center, J. H. Scott, Jr., Director.

The Project Supervisor is K. H. Zaininger, and the Project Scientist is G. W. Hughes. Device processing and radiation testing were performed with the competent assistance of M. Morad. R. Snedeker, and F. Taft. The assistance of J. Fabula and S. Cohen, RCA Solid State Technology Center, Somerville, NJ, in fabricating the hybrid oxides is greatly appreciated.

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## 1. INTRODUCTION

The growth of radiation-hard  $\text{SiO}_2$  for MOS integrated circuits is now within the capability of the semiconductor industry. In spite of this, however, a complete understanding of the basic degradation problem is not yet in hand. Recently work has been reported which illuminates the mechanism of hole transport in  $\text{SiO}_2$ ,<sup>1-3</sup> but an understanding of the atomic and chemical nature of the hole trap and radiation-induced interface state in  $\text{SiO}_2$  is far from complete.

Several models of hole traps have been proposed based upon the short range order of  $\text{SiO}_2$  and band structure considerations. Di-Stephano and Eastman<sup>4</sup> used photoemission spectroscopy to examine the valence-band structure of  $\text{SiO}_2$  and found a narrow band of states near the valence-band edge which they attributed to oxygen non-bonding orbitals. Sigel et al. showed that  $\text{SiO}_2$  films exhibit an  $E'$  center during electron spin resonance measurements which they believe is due to oxygen vacancies near the Si- $\text{SiO}_2$  interface.<sup>5</sup> Sah believes that hole traps are primarily interstitial oxygen vacancies and trivalent silicons.<sup>6</sup> It is also possible that some hole traps and interface states are caused by impurity species within the  $\text{SiO}_2$ . This is

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<sup>1</sup>J. R. Srour, S. Othmer, O. L. Curtis, Jr., and K. Y. Chiu, *IEEE Trans. Nucl. Sci.* NS-23, 1513 (1976).

<sup>2</sup>F. B. McLean, H. E. Boesch, Jr., and J. M. McGarrity, *IEEE Trans. Nucl. Sci.* NS-23, 1506 (1976) and H. E. Boesch, Jr., F. B. McLean, J. M. McGarrity, and G. A. Ausman, Jr., *IEEE Trans. Nucl. Sci.* NS-22, 2163 (1975).

<sup>3</sup>R. C. Hughes, *Bull. Am. Phys. Soc.* 21, 404 (1976).

<sup>4</sup>T. H. DiStephano and D. E. Eastman, *Sol. State Comm.* 9, 2259 (1971).

<sup>5</sup>G. H. Sigel, Jr., E. J. Friebele, R. J. Ginther, and D. L. Griscom, *IEEE Trans. Nucl. Sci.* NS-21, 56 (1974).

<sup>6</sup>C. T. Sah, *IEEE Trans. Nucl. Sci.* NS-23, 1563 (1976).

supported by the many observations that show the difficulty of fabricating consistently hard oxides with a given process.<sup>7,8</sup>

Whatever the nature of hole traps may be, it is clear that they are very process-dependent. For those traps that are deep enough to prevent thermal detrapping, a knowledge of the capture cross section and trap density is sufficient to characterize the radiation response of the oxide. In this report we have measured capture cross sections and trap densities for many different process variations in order to try to understand the process dependence of radiation-hard oxides.

The characterization of hard oxides is usually determined by a flatband or threshold voltage shift after a certain radiation dose, typically  $10^6$  rad. While the voltage shift thus measured is usually assumed to be due mainly to oxide trapped charge, there is evidence to suggest that radiation-induced interface states may play a role that is equally important. It is possible that these interface states may be largely responsible for the wide variation in radiation sensitivity of thermal  $\text{SiO}_2$  grown under similar process conditions.<sup>9</sup> Our recent work in fact shows that hard oxides can be grown in dry oxygen at temperatures ranging from  $900^\circ$  to  $1050^\circ\text{C}$ .<sup>9</sup> In the past it has been assumed that  $1000^\circ\text{C}$  was optimum. This conclusion may have resulted from an occurrence of large numbers of post-irradiation interface states in the oxides grown at other temperatures.

The role that interface states and oxide traps play in determining radiation sensitivity can only be determined by a technique that can separate the two effects. Recently Ning and Yu<sup>10</sup> reported a

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<sup>7</sup>B. L. Gregory, *IEEE Trans. Nucl. Sci.* NS-22, 2295 (1975).

<sup>8</sup>G. W. Hughes and R. J. Powell, *IEEE Trans. Nucl. Sci.* NS-23, 1569 (1976).

<sup>9</sup>G. W. Hughes, "Radiation and Charge Transport in  $\text{SiO}_2$ ," Final Report prepared under Contract N00014-74-C-0185 for Office of Naval Research, July 1977.

<sup>10</sup>T. H. Ning and H. N. Yu, *J. Appl. Phys.* 45, 5373 (1974).

method for studying electron traps in  $\text{SiO}_2$  which has been used by Aitken et al.<sup>11</sup> to measure electron capture cross sections and trap densities of thermal  $\text{SiO}_2$ . In this technique, the measured flatband voltage shift of an MOS capacitor as a function of time during electron injection is used to derive the capture cross section  $S$  and trap density  $N_T$  of oxide traps. This technique was also developed independently by R. J. Powell for capture of holes during the first two quarters of this contract. In addition to this method Powell has developed a current-enhancement technique which gives information about hole traps at both the  $\text{Si-SiO}_2$  and  $\text{gate-SiO}_2$  interface.<sup>12</sup> This current-enhancement phenomenon proves to be a very sensitive measure of the number and location of traps near the  $\text{Si-SiO}_2$  and  $\text{gate-SiO}_2$  interfaces. Furthermore, it provides a tool for comparing radiation sensitivity between samples with different processing histories. Both of the above techniques have been used here in a slightly modified form to draw conclusions about the nature of hole traps in  $\text{SiO}_2$  grown by different processes. The processes that we have examined are: (1) dry oxides grown at temperatures from  $900^\circ$  to  $1150^\circ\text{C}$ ; (2) pyrogenic steam oxides grown at  $875^\circ\text{C}$  and annealed between  $900^\circ$  and  $1100^\circ\text{C}$ ; and (3) pyrogenic hybrid oxides grown at  $925^\circ\text{C}$  and annealed between  $925^\circ$  and  $1150^\circ\text{C}$ .

Section 2 discusses the model used for the trapping kinetics of holes in  $\text{SiO}_2$ , the effects of interface states on measured flatband voltage shifts, and the high field current-enhancement phenomenon. Section 3 discusses the sample preparation techniques and the methods by which the trapping parameters were measured. Section 4 presents the experimental results and makes interpretations about the nature of trapping and interface-state generation from the flatband shift and current-enhancement data. Finally, Section 5 summarizes and concludes with some observations and suggestions for future work.

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<sup>11</sup>J. M. Aitken, D. J. DiMaria, and D. R. Young, *IEEE Trans. Nucl. Sci.* **NS-23**, 1526 (1976).

<sup>12</sup>R. J. Powell, *J. Appl. Phys.* **46**, 4557 (1975).



## 2. HOLE TRAPPING IN SiO<sub>2</sub>

### 2.1 Trapping Kinetics

Consider a distribution of traps in a narrow region near the Si-SiO<sub>2</sub> interface. Let there be  $N_T$  traps per cm<sup>2</sup> of which  $N_T^+$  traps per cm<sup>2</sup> are filled with holes. Then the trapping probability of a hole reaching the interface is  $(N_T - N_T^+) S$ , where  $S$  is the capture cross section for holes. Letting  $J$  be the constant hole current density flowing through the interface, we can write:

$$\frac{dN_T^+}{dt} = \frac{J}{q} (N_T - N_T^+) S \quad (1)$$

This equation has the solution:

$$N_T^+ = N_T \left( 1 - e^{-\frac{JS t}{q}} \right) \quad (2)$$

and if we express the densities of traps in terms of flatband shift, equation (2) becomes:

$$\Delta V_{FB} = \Delta V_{FBF} \left( 1 - e^{-\frac{JS t}{q}} \right) \quad (3)$$

where  $\Delta V_{FB} = (qN_T^+ d_{ox})/\epsilon_{ox}$  is the flatband shift at time  $t$ ,  $d_{ox}$  is the oxide thickness,  $\epsilon_{ox}$  is the dielectric constant, and  $\Delta V_{FBF} = (qN_T d_{ox})/\epsilon_{ox}$  is the flatband shift with all the traps filled. This simple model assumes that emission from traps is unimportant. One can determine the trap density  $N_T$  and the capture cross section  $S$  by fitting equation (3) to experimental data. Unfortunately, it is not always possible to measure  $\Delta V_{FBF}$  directly because tunnel injection may prevent complete filling of traps, and the highest value of  $\Delta V_{FB}$  reached may be appreciably less than  $\Delta V_{FBF}$ . More importantly, radiation-induced interface states at saturation can account for a substantial amount of positive or negative charge making a determination of  $N_T$  from  $\Delta V_{FBF}$  difficult.

There are several alternate ways of determining  $N_T$  and  $S$  from the data. Consider the derivative of equation (3):

$$\frac{d}{dt} \Delta V_{FB} = \Delta V_{FBF} e^{\frac{-JSt}{q}} \left( \frac{JS}{q} \right) \quad (4)$$

Equation (4) at  $t = 0$  gives the product  $N_T S$ , e.g.,

$$\left| \frac{d}{dt} \Delta V_{FB} \right|_{t=0} = \Delta V_{FBF} \frac{JS}{q} = J \frac{d_{ox}}{\epsilon_{ox}} (N_T S) \quad (5)$$

Also taking the log of equation (4) gives

$$\ln \left[ \frac{d}{dt} \Delta V_{FB} \right] = \ln \left[ \frac{J d_{ox}}{\epsilon_{ox}} (N_T S) \right] - \frac{JS}{q} t \quad (6)$$

Therefore the slope of equation (6) on a semi-log plot yields the capture cross section  $S$ . This technique is also limited to situations in which interface-state charge is a small fraction of oxide-trapped charge, that is, early in the irradiation. For hard oxides in which the amount of oxide-trapped charge is small, this may mean measuring many flatband shifts to a high degree of accuracy during the first few seconds of exposure.

Another alternative which gives less precise results but makes measurements more feasible is to use equation (5) to determine the product  $N_T S$  and then extract  $N_T$  from  $\Delta V_{FBF}$  by putting upper and lower bounds on it. This can be done by measuring the flatband voltage at two points where either all the acceptor or all the donor interface states are charged.

## 2.2 Effect of Interface States on Measured Flatband Voltage

Consider the band diagram shown in figure 1(a). The surface is in accumulation and the Fermi level is at the conduction band edge. All acceptor interface states will be charged negatively as shown and all donors will be neutral. Thus, the total flatband shift

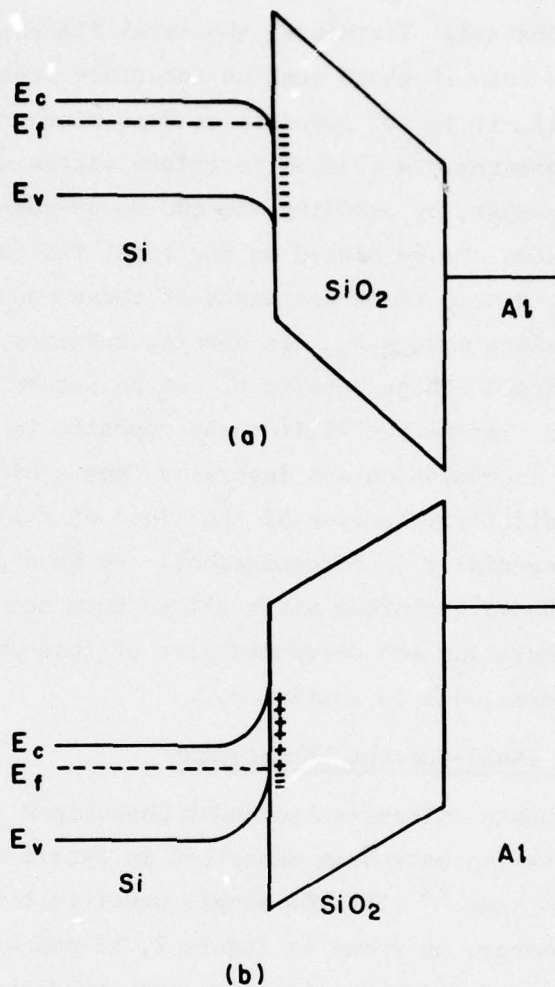


Figure 1. Band diagram of Si-SiO<sub>2</sub> MOS capacitor. (a) In accumulation, only acceptor interface-state charged; (b) in inversion, mostly donors are charged.

$\Delta V_{FB}$  will be more positive than if there were no interface states (oxide charge is positive). On the other hand, if the silicon surface is inverted as shown in figure 1(b), the Fermi level is near the valence-band edge, all donors above the Fermi level will be charge, and all acceptors neutral. Between the Fermi level and the valence band the opposite situation will prevail, but as a first-order estimate *mostly*



donors will be charged. Therefore, the total flatband shift  $\Delta V_{FB}$  will be more negative than if there were no interface states present.

In general, it is not possible to determine from capacitance-voltage (C-V) measurements whether interface states are donors or acceptors.<sup>13</sup> However, by assuming the two worst-case situations outlined above, bounds can be placed on the total flatband shift and we can determine  $N_T$  within the constraints of these bounds. For example, if all the interface states  $N_{SS}$  are donors, then for n-type silicon the actual oxide-trapped charge density  $N_T^+$  can be determined by measuring  $\Delta V$  at inversion. For p-type silicon the opposite is of course true. Measuring  $\Delta V$  at accumulation and inversion from a high-frequency C-V (HFCV) plot is difficult because of the slope of the C-V curves at these points (especially at accumulation). We have devised a deep-depletion C-V (DDCV) technique which allows more accurate measurement of  $\Delta V_{FB}$  at accumulation and overcomes part of this problem. This method will be discussed in section 3.2.

### 2.3 High Field-Current Enhancement

The basic current-enhancement phenomenon and its experimental implementation have been described in detail elsewhere and will only be outlined here.<sup>12</sup> The MOS sample under test is placed in a vacuum monochromator, as shown in figure 2, biased with an appropriate gate bias, either positive or negative, and irradiated with vacuum ultraviolet (VUV) light of a photon energy that is strongly absorbed\* in the oxide film. The time dependence of the total current flowing through the MOS device is measured. The current measured at the initiation of radiation is just the electron or hole photocurrent flowing through the oxide. If the applied field is sufficient, eventually a

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<sup>13</sup>G. W. Hughes, *J. Appl. Phys.* 48, 5357 (1977).

\*This is not essential, and the device may be irradiated with penetrating radiation as well.

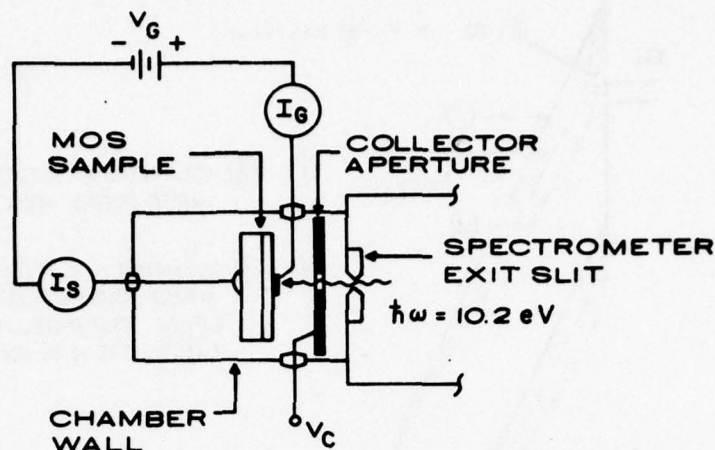


Figure 2. Experimental arrangement used for hole transport studies.

current enhancement will be observed as holes accumulate near the negatively biased electrode, and the interface field increases enough to allow Fowler-Nordheim tunneling of electrons to occur. The mechanism of current enhancement is depicted schematically in figures 3 and 4. Figure 3 shows the band diagram for  $\text{SiO}_2$  as irradiation progresses. Initially the field throughout the  $\text{SiO}_2$  is approximately the applied field, which must be  $\gtrsim 5$  MV/cm for current enhancement to occur. This is to ensure that any holes trapped at the Al interface do not perturb the field there enough to decrease the net hole generation through geminate recombination. During this time the net hole generation is constant, and the measured photocurrent does not change with time as figure 4 shows. As the density of trapped holes builds up at the silicon interface, the bands bend as shown in figure 3 until the barrier becomes thin enough for tunneling to occur. At this point, marked ① in figure 4, the total current increases as more holes are trapped and the bands are bent even further, resulting in even more tunneling current. In the absence of interface states, this situation continues until equilibrium is reached when the number of holes trapped per unit time is just balanced by the number annihilated by the tunneling electrons. This is marked ② in figure 4 as the current approaches

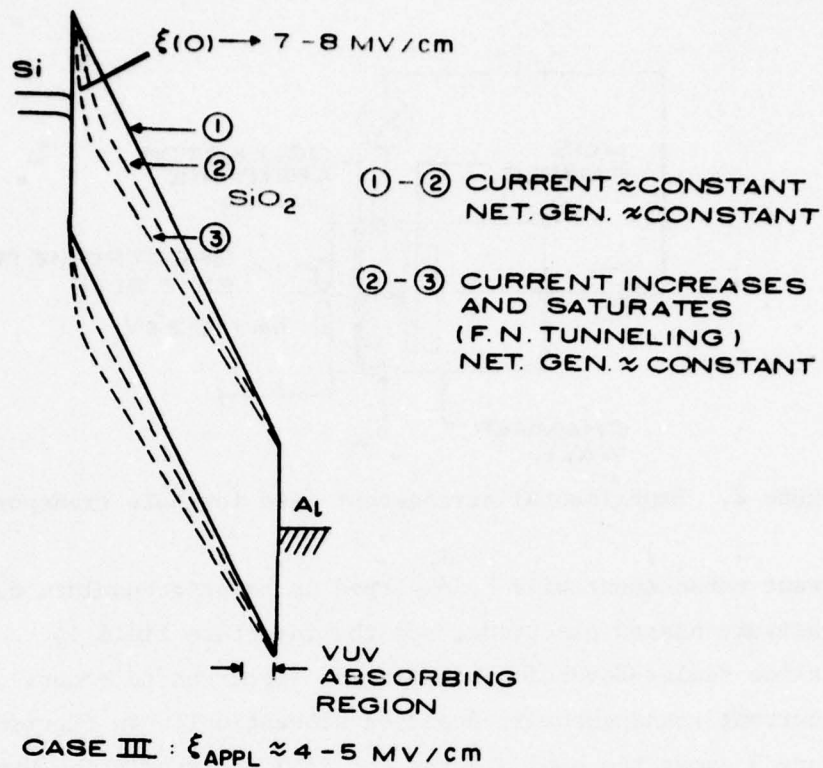


Figure 3. Energy band diagram of an Si-SiO<sub>2</sub> MOS structure with high applied field.

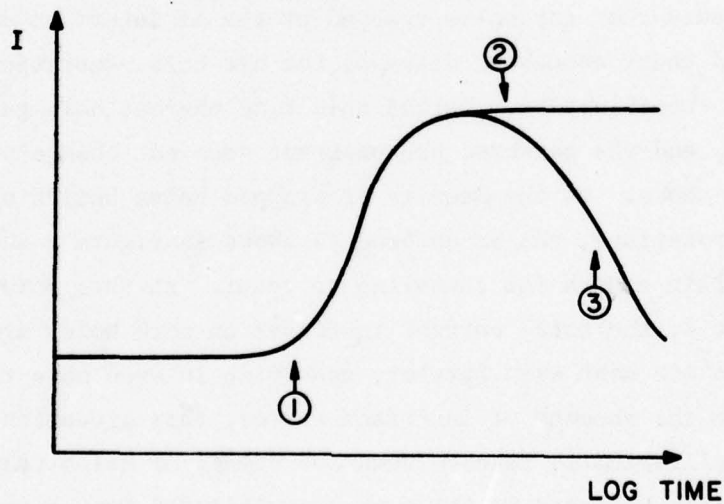


Figure 4. Behavior of measured current vs time under bias conditions shown in fig. 3. Numbers refer to discussion in text.



saturation. In some samples, instead of saturating, the current actually begins to decrease as time goes on. One might speculate that this is due to a decrease in the net number of trapped holes as electrons tunneling in from the silicon annihilate them. However, this would have a self-limiting effect since as the net hole density decreases, the interface field and hence the tunneling current would decrease until equilibrium was reached. Actually, equilibrium would be established before the current had a chance to decrease and situation ② would prevail. The most probable explanation for this decreasing current phenomenon is that acceptor-type interface states are generated near the interface and partially compensate the field enhancement due to hole trapping. This hypothesis is illustrated in figure 5. Here we show the band diagram at the Si-SiO<sub>2</sub> interface under three different conditions. Condition I shows the SiO<sub>2</sub> conduction band edge under an oxide field of 5 MV/cm with no oxide charge or interface states. Condition II includes a positive sheet of oxide charge of  $5 \times 10^{12} \text{ cm}^{-2}$  50 Å from the Si-SiO<sub>2</sub> interface, and condition III includes both the positive oxide charge and a negative sheet of interface states 10 Å from the interface of the same magnitude as the oxide charge. The location and magnitude of the positive charge is reasonable and is based upon measurements of charge centroids<sup>11,14</sup> and our current-enhancement data. The location of the interface-state centroid at 10 Å from the silicon interface is not unreasonable especially for midgap states.<sup>15</sup> The magnitude of this charge is based upon the deep-depletion C-V measurements shown below.

<sup>14</sup>R. J. Powell and G. W. Hughes, "Radiation and Charge Transport in SiO<sub>2</sub>," Annual Report prepared under Contract N00014-74-C-0185 for Office of Naval Research, January 1975.

<sup>15</sup>F. P. Heiman and G. Warfield, *IEEE Trans. Electron. Devices* **ED-12**, 167 (1965).

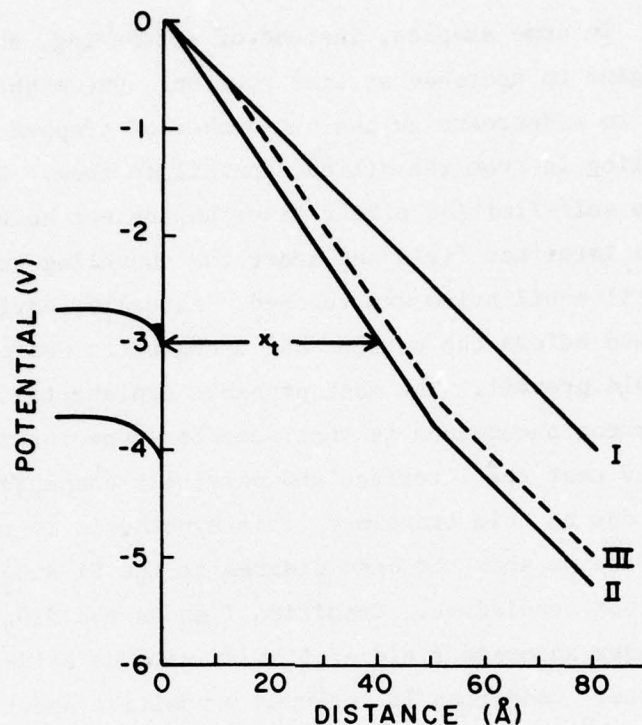


Figure 5. Band diagram of Si-SiO<sub>2</sub> MOS interface showing the effect of positive and negative sheet on band bending and tunneling distance. Roman numerals refer to discussion in text.

In condition I, no current enhancement results because the tunneling distance  $x_t \approx 60 \text{ Å}$ . In condition II, the positive sheet charge increases the interfacial field to 7.5 MV/cm, and decreases the tunneling distance to 40 Å allowing large enhancement currents to flow. In condition III, the negative interface-state charge compensates the positive oxide charge and the tunneling distance  $x_t$  increases to  $\approx 42 \text{ Å}$ . Since the tunneling current depends exponentially upon barrier width, this results in a decrease in current by at least an order of magnitude.<sup>12</sup>

Current enhancement is also a very useful tool for probing the hole traps at the Al-SiO<sub>2</sub> interface where there is no counterpart to

flatband shift measurements. The current enhancement at this interface is solely a function of the applied field and trap density. Interface states do not exist here, so that the interpretations are simplified. In section 4.2 we present some interesting results using this technique.



### 3. EXPERIMENTAL METHODS

#### 3.1 Sample Preparation

Oxide films were thermally grown on n- and p-type 5 to 10 ohm-cm (100) silicon slices by three different processes. These processes are summarized in table I.

TABLE I. PROCESSING CONDITIONS

<u>Oxidation Process</u>	<u>Oxidation Temperature (°C)</u>	<u>Anneal Temp (15 min)</u>	<u>Nominal Oxide Thickness (Å)</u>
Dry (p-type)	900 } 1000 } 1150 }	Half annealed in Ar at 800°C, half unannealed	750
Pyrogenic Steam (100%) (n-type)	875	900°C to 1100°C in He	1000
Hybrid (30-min 100% pyrogenic with 3% HCl steam 60-min dry O <sub>2</sub> (n-type)	925	925°C <i>in situ</i> in N <sub>2</sub>	750

Pyrogenic steam is nothing more than steam produced by burning hydrogen inside the furnace tube. With adjustment of the ratio of H<sub>2</sub> to O<sub>2</sub>, the steam content can be varied from 0 to 100%. The advantages of this method are (1) the percentage steam can be controlled accurately, (2) the purity of the steam is determined solely by the purity of the gases, and (3) the steam can be quickly and easily shut on and off, making hybrid oxides possible.

All of these wafers were metallized with 1-mm-diameter semi-transparent aluminum dots approximately 100 Å thick. The aluminum was evaporated from an In Source<sup>®</sup> induction-heated crucible source and in all cases resulted in less than 0.1-V shift under a standard bias-temperature C-V test (CVBT;  $\pm 10$  V at 300°C for 5 min).

For comparison purposes all wafers used in the capture cross-section study were also irradiated with 1-MeV electrons under 1-MV/cm positive bias to a dose of  $10^6$  rad. The results of this test are shown in figures 6, 7, and 8. All flatband shifts are normalized by a square law thickness dependence to  $750 \text{ \AA}$ . As the figures show, some of the oxides are relatively hard and some of them, not being grown by an optimum process, are very soft. This wide range of radiation sensitivities is desirable in that it provides us with a wide range of process-induced trapping situations for study. The inclusion of a hard oxide from each of the three processes also provides us with a benchmark for comparison of the other oxides.

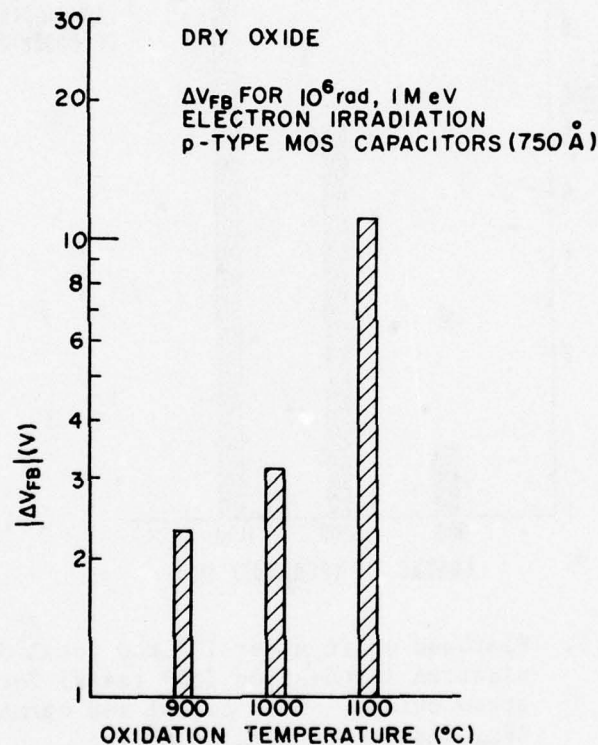


Figure 6. Flatband shift after  $10^6$  rad total dose 1-MeV electron irradiation ( $10^4$  rad/s) for dry oxides.

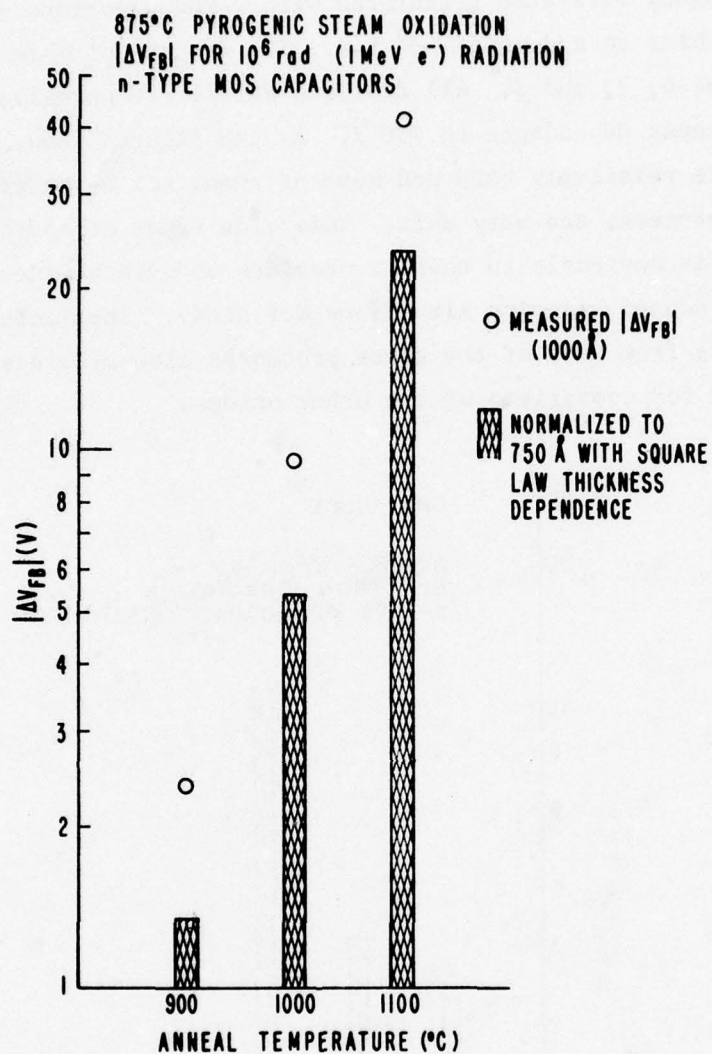


Figure 7. Flatband shift after  $10^6$  rad total dose 1-MeV electron irradiation ( $10^4$  rad/s) for pyrogenic steam oxides. Both actual and normalized  $\Delta V_{FB}$  data shown ( $\Delta V_{FB} \propto d_{ox}^2$ ).



HYBRID OXIDATION { 60 MIN PYROGENIC STEAM/3% HCl  
 { 30 MIN DRY O<sub>2</sub>

$|ΔV_{FB}|$  FOR  $10^6$  rad (1 MeV e<sup>-</sup>) TOTAL DOSE  
 n-TYPE MOS CAPACITORS (750 Å)

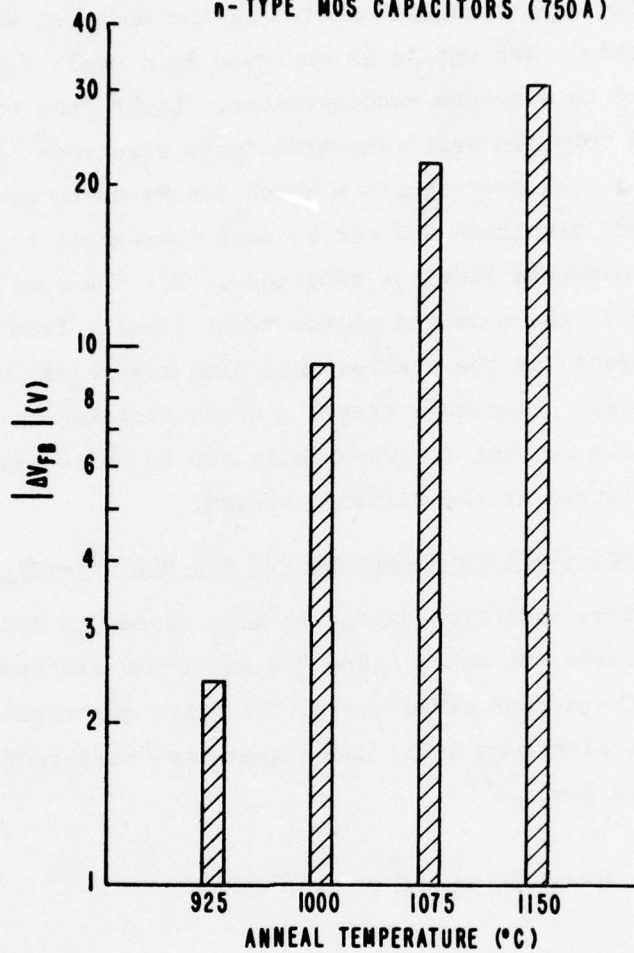


Figure 8. Flatband shift after  $10^6$  rad total dose 1-MeV electron irradiation ( $10^4$  rad/s) for hybrid oxides.

### 3.2 Measurement Techniques

#### 3.2.1 Hole Photocurrents

All MOS capacitors were irradiated with 10.2-eV VUV light in a VUV spectrometer. The experimental arrangement is shown in figure 2 with the electronics connected in the mode for measuring the hole photocurrents. The sample is enclosed in a small vacuum chamber coupled directly to a vacuum monochromator. Light from the monochromator is directed onto the semitransparent gate electrode of the MOS sample through a collector aperture which functions to confine the light to the gate electrode and can be used to measure the magnitude of emission into vacuum from the electrode. For the bias polarity shown in figure 3, the measured photocurrent results from electron-hole pairs generated in the shallow absorbing region of the  $\text{SiO}_2$  near the gate electrode. Electrons travel a short distance to be collected at the gate so the current is essentially due to holes traversing the oxide to be collected at the silicon cathode.

#### 3.2.2 Dose Comparison Between VUV and High Energy Irradiation

Since radiation damage in  $\text{SiO}_2$  is due to holes being trapped in the oxide, we can compare VUV and 1-MeV electron irradiation by calculating the number of hole-electron pairs generated per second.

For 1-MeV electrons it is known that the "mean range" of a 1-MeV electron in  $\text{SiO}_2$  is<sup>16</sup>

$$R = 3.84 \text{ mg/cm}^2 \quad (9)$$

The density of  $\text{SiO}_2$  is  $2.3 \text{ g/cm}^3$  so that the actual absorption depth is

$$L_A = 0.169 \text{ cm} \quad (10)$$

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<sup>16</sup>L. Katz and A. S. Penfold, *Rev. of Modern Physics* 24, 28 (1952).

Defining  $\beta = \frac{L_A}{E_s}$  where  $E_s = 1$  MeV, then,

$$\beta = 1.69 \times 10^{-7} \text{ cm/eV} \quad (11)$$

Assuming a pair formation energy  $E_p$ , the length required to create one electron-hole pair is  $\beta E_p$ . The total number of electron-hole pairs/cm<sup>2</sup> created in an oxide of thickness  $d_{ox}$  after a dose of  $\phi$  rad is then

$$N_p = \alpha \phi \frac{d_{ox}}{\beta E_p} \quad (12)$$

where  $\alpha = 3 \times 10^{-7}$  MeV electrons/cm<sup>2</sup>/rad.

Strour et al.<sup>17</sup> have estimated  $E_p \approx 19$  eV. Therefore, for a 750-Å-thick oxide and a dose of  $10^6$  rad,

$$N_p = 6.96 \times 10^{13} \text{ cm}^{-2} \quad (13)$$

For VUV irradiation, Powell has shown that the initial hole photocurrent and thus the quantum yield  $Y$  saturates with  $Y$  near 100% as the oxide field approaches 5 MV/cm because of the reduction of geminate recombination.<sup>12</sup>

For the light intensity and electrode area that we use, we find the hole photocurrent at 5 MV/cm is typically

$$J_{ph} \approx 5.1 \times 10^{-8} \text{ A/cm}^2 \quad (14)$$

Thus, the number of electron-hole pairs created by the VUV per cm<sup>2</sup> per second is

$$\frac{J_{ph}}{q} = 3.18 \times 10^{11} \text{ s}^{-1} \text{ cm}^{-2} \quad (15)$$

The total number for  $t$  in seconds is then

$$N_p = \frac{J_{ph}}{q} t \quad (16)$$

<sup>17</sup>J. R. Strour, O. L. Curtis, and K. Y. Chiu, *IEEE Trans. Nucl. Sci.* NS-21, 73 (1974). For analysis of data in preceding reference, see G. A. Ausman, Jr. and F. B. McLean, *Appl. Phys. Letters* 26, 173 (1975).



So from equation (13) and (16) we find  $t \approx 218$  s for an equivalent 1-Mrad VUV dose.

### 3.2.3 Deep-Depletion C-V Measurements

Flatband shifts during irradiation were measured by both a high-frequency C-V (HFCV) technique and a deep-depletion C-V (DDCV) technique. In the high-frequency technique, the capacitor is irradiated for a length of time at a positive bias, the radiation is removed, and a 1-MHz HFCV curve is taken. The whole procedure takes about 20 s. In the DDCV technique, a bias is applied during the irradiation as shown in figure 9. With a small sampling resistor,  $R_S$ , the current is calculated by measuring the voltage  $V_S(t)$  as shown in figure 9. When a DDCV measurement is desired, the bias is rapidly swept down to a preset negative voltage and back, the whole sweep taking about 100  $\mu$ s. During this time the UV can be either on or off as it does not affect the measurement. The method is similar to a quasi-static C-V measurement except that the sweep rate of the ramp voltage is very high. Under steady-state conditions, the capacitor is biased far into accumulation at  $+V_B$ . At the moment the DDCV curve is needed, a high sweep-rate negative-going ramp is initiated which sweeps to  $-V_I$  and then retraces at the same rate back to  $+V_B$ . If  $\alpha$  is the sweep rate of the ramp, then, neglecting  $R_S$ , the current through the capacitor is

$$I = C(V_g) \frac{dV_g}{dt} = \alpha C(V_g) \quad (17)$$

and

$$V_S = IR_S = \alpha R_S C(V_g) \quad (18)$$

Time is related to  $V_g$  through the relationship  $V_g = \alpha t$  so that the time scale can be quickly converted to a voltage scale.

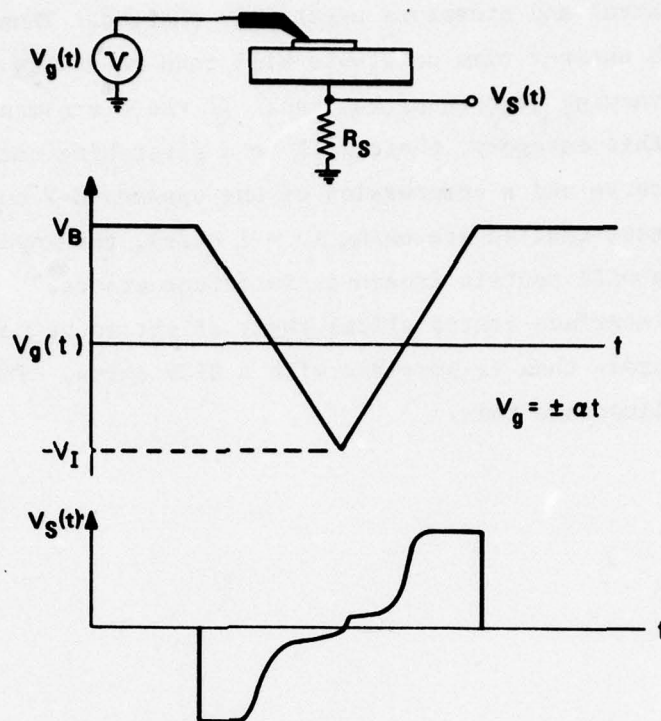


Figure 9. Deep-depletion C-V measurement technique showing circuit connections and voltage waveforms.

Without interface states, the above system gives an accurate replica of a deep-depletion C-V curve. The majority carriers are in equilibrium with the ramp voltage as long as the sweep time is long compared with the geometrically modified dielectric-relaxation time of the MOS capacitor.<sup>18</sup> The minority carriers are "frozen-out" for moderate to high slew rates. When interface states are present, the response of the capacitor is slightly different. Interface states with time constants long compared with the sweep time will be "frozen in" with the Fermi level at the conduction band point. That is, donors

<sup>18</sup>G. W. Hughes and R. M. White, *IEEE Trans. Electron. Devices* **ED-22**, 945 (1975).

will be neutral and acceptors negatively charged. Those interface states with shorter time constants will tend to follow the voltage ramp with varying degrees of success. If there are many interface states in this category, there will be a stretching out of the down-sweep C-V curve and a compression of the up-sweep C-V curve.<sup>19</sup> For the sweep rate that we are using ( $\alpha = 1$  MV/s), the lower 0.7 eV of the bandgap will contain frozen-in interface states.<sup>20</sup> This freezing-in of the interface states allows their effect to be measured much more accurately than is possible with a HFCV curve. The data in section 4.1 illustrate this.

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<sup>19</sup>J. G. Simmons and L. S. Wei, *Solid State Electronics* 16, 53 (1973).

<sup>20</sup>S. M. Sze, *Physics of Semiconductor Devices* (John Wiley & Sons, New York, 1969), p. 455.



#### 4. MEASURED HOLE CAPTURE CROSS SECTION AND TRAP DENSITIES

##### 4.1 Interpretation of $\Delta V_{FB}$ vs t Data

Using the techniques described in section 3, we irradiated MOS capacitors on the oxides shown in table I and measured the flat-band shifts as a function of time. From these data, the capture cross section and trap density were determined.

At the beginning of the irradiation the initial probability of capture  $P_{co}$  is given by

$$P_{co} = N_T S \quad (19)$$

From equation (5) this is

$$P_{co} = \frac{C_{ox}}{I_o} \frac{d}{dt} [\Delta V_{FB}]_{t=0} \quad (20)$$

where  $C_{ox}$  is the actual oxide capacitance and  $I_o$  is the initial photocurrent.

For  $t \ll q/JS$ , equation (3) shows that

$$\Delta V_{FB} \approx \frac{I_o}{C_{ox}} P_{co} t \quad (21)$$

This equation can safely be used to measure  $P_{co}$  directly as long as the measured  $\Delta V_{FB}$  versus  $t$  is linear in  $t$ . For example, in our experiments it is difficult to determine exposures accurately for less than 1 s, and it becomes increasingly difficult to resolve small flat-band shifts for very short exposures. Consequently, our measurement technique consists of the following procedure. The sample is exposed for 1 s, a DDCV curve taken, the sample allowed to relax for 60 s, and a DDCV curve is taken again. This allows any transporting charge to move completely through the oxide. The sample is exposed again for another 1 s and the whole process repeated. An example of the resulting

flatband shifts before and after relaxation is shown in figure 10. This is an 875°C pyrogenic oxide annealed at 900°C in helium. The bias during irradiation is +5 MV/cm. (This particular bias was used during most of the measurements because it is the bias needed to interpret the current enhancement data.) The probability of capture was measured for other biases and was found to be bias-dependent. This will be discussed below. This particular sample had about 0.04-V shift due solely to transporting charge which disappeared after the capacitor was allowed to relax. Other samples showed less of a discrepancy between the initial and relaxed  $\Delta V_{FB}$ . Note also that the slope of  $\Delta V_{FB}$  versus  $t$  is 1.0 on a log-log scale which validates the assumptions made for equation (21). From this figure and equation (21), we find  $P_{co} = N_T S = 0.02$ .

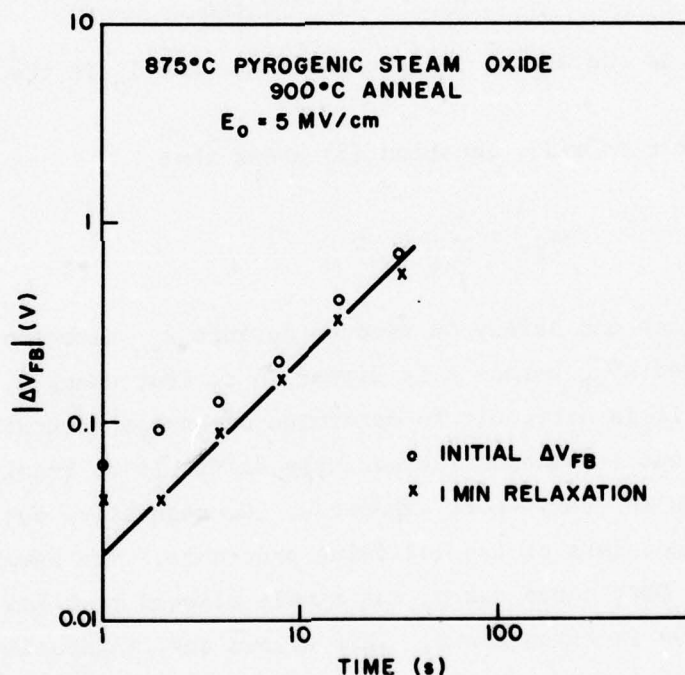


Figure 10. Initial  $|\Delta V_{FB}|$  vs  $t$  data for pyrogenic steam oxide annealed at 900°C, showing relaxation effect and resulting unity slope line.

After the probability of capture is measured, what remains to be determined is  $N_T$  or  $S$  from the  $\Delta V_{FB}$  versus  $t$  data. As explained above, because of the relative inaccuracy in our measurement technique, it is not possible to use equation (6) to measure the capture cross section  $S$ . Instead, we measured  $\Delta V$  versus  $t$  by both HFCV and DDCV techniques and determined bounds on  $\Delta V_F$  from these measurements. Figure 11 shows these measurements for the same sample as in figure 10. This figure contains three sets of data, the DDCV data measured from accumulation (+5 MV/cm), and the HFCV data measured at flatband and inversion. As the figure shows, for  $t \gtrsim 250$  s, the DDCV curve begins to deviate from the HFCV curve and eventually reverses. The deviation between the curves shows that interface states are being created between the flatband Fermi level and silicon conduction band. However, it is not possible to determine whether these states are donors or acceptors.<sup>13</sup> The reversal of the DDCV curve implies one of two things. (1) The oxide trapped charge  $N_T^+$  is being annihilated by electrons tunneling in from the silicon under high fields (see fig. 3). This must be accompanied by an increase in the number of donor interface states above the flatband Fermi level  $E_F$  which must compensate both the annihilated  $N_T^+$  and all acceptor  $N_{SS}$  below  $E_F$ . (2) The net oxide-trapped charge  $N_T^+$  does *not* decrease with time but the number of acceptor  $N_{SS}$  throughout the bandgap increases and becomes greater than  $N_T^+$  (see section 2.2).

For the reasons given in section 2 we believe the second scenario is the most probable one, but in either case the reversal can be used to set a lower bound on  $N_T$ , the number of fillable traps. The Fermi level is at the conduction band when the DDCV measurement is initiated, so that in either case only acceptor interface states are charged and  $\Delta V_{FB}$  due to  $N_T$  is at least as large as the maximum shown.



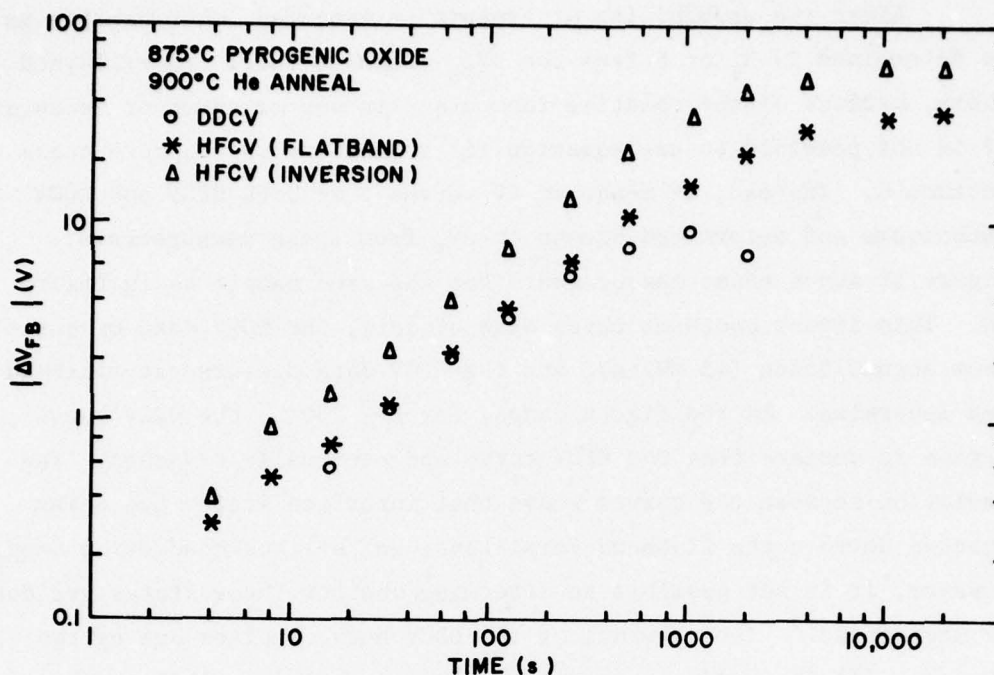


Figure 11. Complete  $|\Delta V_{FB}|$  vs  $t$  data for pyrogenic steam oxide annealed at 900°C showing differences between DDCV and HFCV techniques. 5-MV/cm bias.

The upper limit on  $N_T$  is of course determined by the saturated C-V shift at inversion. Here the Fermi level is near the silicon valence band, all the donors above  $E_F$  are charged positively, and any acceptors between  $E_V$  and  $E_F$  are charged negatively. Presumably, the net interface charge in this case would be positive. This being the case, the  $\Delta V$  due to  $N_T$ , the number of fillable traps, is no larger than that measured at inversion.

These two cases give us limits on  $N_T$  through the equation

$$N_T = \frac{\epsilon_{ox}}{qd_{ox}} |\Delta V_F| \quad (22)$$

where  $\epsilon_{ox}$  and  $d_{ox}$  are the permittivity and thickness of the  $\text{SiO}_2$  and  $q$  is the magnitude of the electronic charge. From the upper and lower limit on  $N_T$ , lower and upper limits on  $S$  can be computed from equation (19). This was done for some of the oxides shown in table I for applied oxide fields  $E_o$  of 1, 3, and 5 MV/cm. The data from these measurements are shown in appendix A. The results of the capture cross section and trap density calculations are shown in figures 12, 13, and 14 for  $E_o = 1$  MV/cm. While capture cross-section data do not provide any definitive answers about the nature of hole traps, such data can be useful for comparing oxides of different degrees of hardness. For the oxides grown for this study, the degree of hardness ranges from very hard to very soft depending upon the particular process used. It would be useful then to know if the capture cross sections for the very hard and very soft oxides are quite different, suggesting a different hole trap, or if they are the same, suggesting perhaps only a difference in trap density.

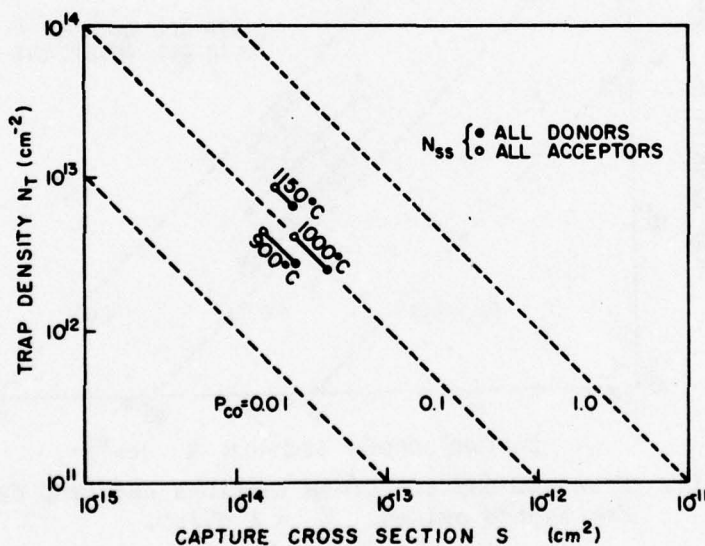


Figure 12. Measured capture cross sections and trap densities for unannealed dry oxides.  $E_o = 1$  MV/cm.

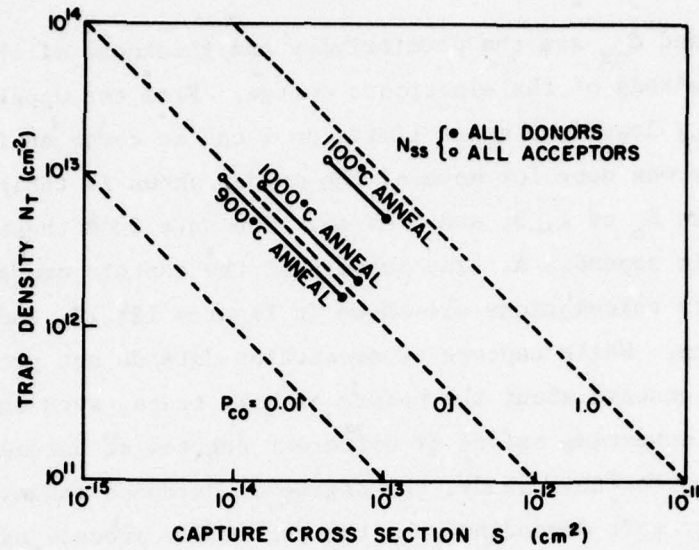


Figure 13. Measured capture cross sections and trap densities for pyrogenic steam oxides.  $E_0 = 1$  MV/cm.

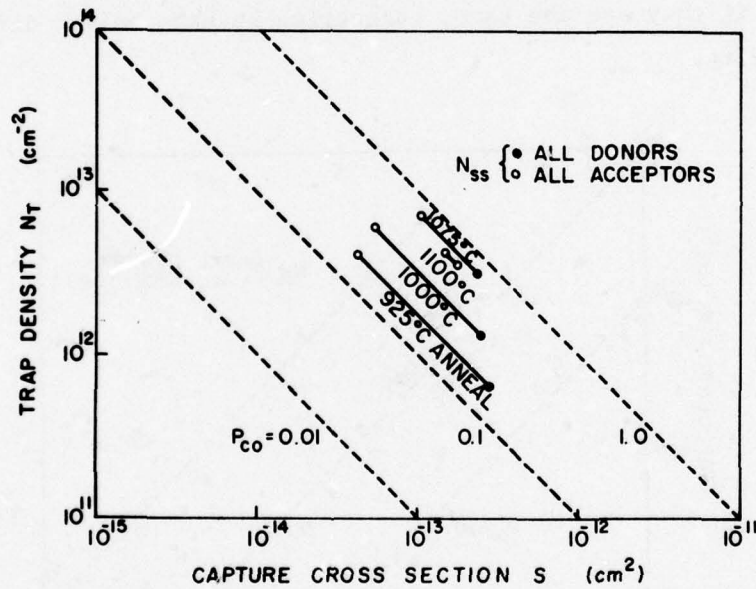


Figure 14. Measured capture cross sections and trap densities for hybrid oxides.  $E_0 = 1$  MV/cm.



For the unannealed dry oxides shown in figure 12, it can be seen that the spread in  $N_T$  is relatively small, indicating not too many interface states. The initial probability of capture is  $\sim 0.1$  for all three oxidations, even though the high-energy 1-Mrad radiation data in figure 6 show a factor of 5 difference in  $\Delta V_{FB}$  between 900° and 1000°C hard oxides and the 1150°C soft oxide. In addition the DDCV data shown in appendix A indicate no current reversal and therefore few acceptor interface states. However, the spread in  $N_T$  indicates *some* interface states present which would suggest that they are mainly donors. The capture cross section  $S$  for these oxides is  $\sim 5 \times 10^{-14} \text{ cm}^2$ .

The pyrogenic steam oxides in figure 13 show a much wider spread in  $N_T$  indicating many more interface states than the dry oxides. The DDCV data in the appendix show a current reversal, indicating acceptor interface states present. Since we know nothing about the donors, we cannot say exactly where on the constant  $P_{co}$  lines the data actually lie. Here the capture cross section for the oxide traps is less certain but appears to lie between  $5 \times 10^{-14}$  and  $10^{-13} \text{ cm}^2$  for all the oxides taken as a whole. As figure 7 shows, the  $\Delta V_{FB}$  for high-energy irradiation of these samples ranges over more than an order of magnitude. The 900°C annealed oxide shows a very acceptable 1.3-V shift in figure 7, but as figure 13 shows, the  $P_{co}$  is not much different from the soft 1000°C annealed oxide. The differences in hardness shown in figure 7 are probably due mainly to interface states.

The pyrogenic hybrid oxides shown in figure 14 are somewhat anomalous when compared with the dry and steam oxides of figures 13 and 14. The range of possible capture cross sections for the dry and steam oxides overlap enough that we might conclude that the trap involved in all cases is the same and that only the density of traps and interface states are different between the oxides. With the hybrid oxides, however, it becomes increasingly difficult to stretch this argument. Here it appears that a trap with  $S \sim 2 \times 10^{-13} \text{ cm}^2$  could explain all the hybrid data. This is four times larger than that

assumed for the dry oxides. The significant thing about the hybrid data is that the main difference between the 925°C annealed hard oxide (see fig. 8) and the soft oxides is the density of traps and interface states. The capture cross section ranges for all hybrid oxides overlap completely. Here again, as shown for the hard pyrogenic steam oxide, the hard hybrid oxide has a substantial number of interface states. The data in the appendix show that many of these are acceptors, and they therefore must provide a certain amount of compensation for the trapped holes.

The range of uncertainty in  $N_T$  and  $S$  is delineated in figures 12, 13, and 14. The uncertainty in  $P_{co}$  is not shown here but could be as high as  $\pm 50\%$  for the worst case. Even at this extreme it is not possible to reconcile all oxides measured and show them as having only one capture cross section. What is significant, however, is that all the dry oxides and the 900° to 1000°C annealed pyrogenic oxides have traps with about the same cross section. This suggests that hole traps in wet and dry oxides are the same. The differences in hardness measured could then be explained by differences in trap density and interface state density alone. The oxides that do not fit in this category may have some sort of impurity-related trap in addition to the *intrinsic* trap of the hard oxides. The hybrid oxides were in fact grown in an ambient of 3% HCl which may very well change the structure of the oxide as well as the trap capture cross section.

The capture cross sections of these hole traps were measured with an oxide field  $E_o$  of 1 MV/cm (which is the normal bias field) and  $E_o = 5$  MV/cm (which is the field used for current enhancement). Much to our surprise, the capture cross section was found to be field-dependent so that  $S \propto E_o^{-1}$ . This is shown in figure 15 for the 1000°C dry oxide (unannealed). We have actually shown  $P_{co}$ , the initial probability of capture here, but, as shown in figure 16,  $\Delta V_{FBF}$  is field-independent, so it is actually  $S$  which is field-dependent in  $P_{co}$ . The

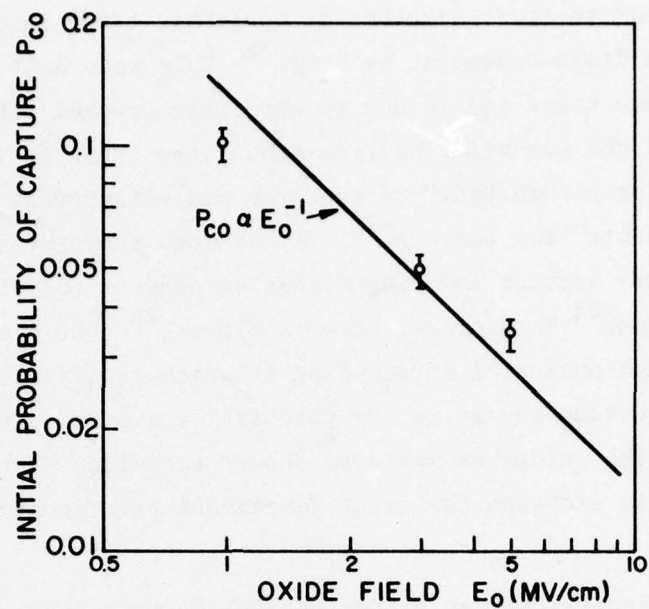


Figure 15. Field dependence of initial probability of capture for unannealed 1000°C dry oxide.

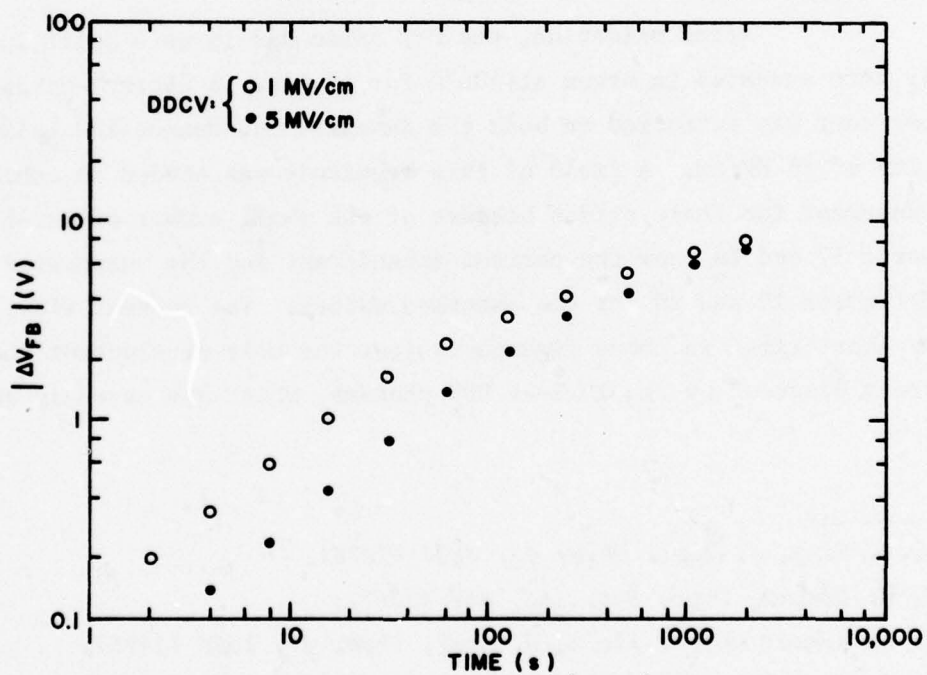


Figure 16. Field dependence of  $|\Delta V_{FB}|$  vs  $t$  data for unannealed 1000°C dry oxide.



electron capture cross sections of coulombic traps in  $\text{SiO}_2$  have been shown to be field-dependent by Ning.<sup>21</sup> This is a well known phenomenon for coulombic traps and is due to the Poole-Frenkel effect or field lowering of the potential barrier around the trap.<sup>22</sup> This decreases the "sticking probability" of the trap and effectively decreases the "critical orbit" for capture.<sup>21</sup> It has been shown by Arnett and Klein that the same barrier lowering mechanism plays a role in capture by neutral traps.<sup>23</sup> They argue, after Jonscher,<sup>24</sup> that a neutral trap has a short-range potential surrounding it which is affected by the applied field in the same way as is the potential surrounding the coulombic trap. All the oxides we measured showed a similar decrease in  $S$  with applied field although the exact functional relationship has not been determined.

#### 4.2 Interpretation of Current-Enhancement Data

##### 4.2.1 Dry Oxides

After oxidation, the dry oxide wafers were split in half; half were annealed in argon at  $800^\circ\text{C}$  for 15 min. A current-enhancement experiment was performed on both the annealed and unannealed oxide fields of  $\pm 6$  MV/cm. A field of this magnitude was needed to achieve enhancement for these oxides because of the small number of oxide traps. Figures 17 and 18 show the current enhancement for the unannealed oxides and figures 19 and 20 for the annealed oxides. The current flowing for very short times in these figures is just the hole or electron photo-current produced by the 10.2-eV VUV photons, which are strongly absorbed

<sup>21</sup>T. H. Ning, *J. Appl. Phys.* 47, 3203 (1976).

<sup>22</sup>J. G. Simons, *Phys. Rev.* 155, 657 (1967).

<sup>23</sup>P. C. Arnett and N. Klein, *J. Appl. Phys.* 46, 1400 (1975).

<sup>24</sup>A. K. Jonscher, *Thin Solid Film* 1, 213 (1967).

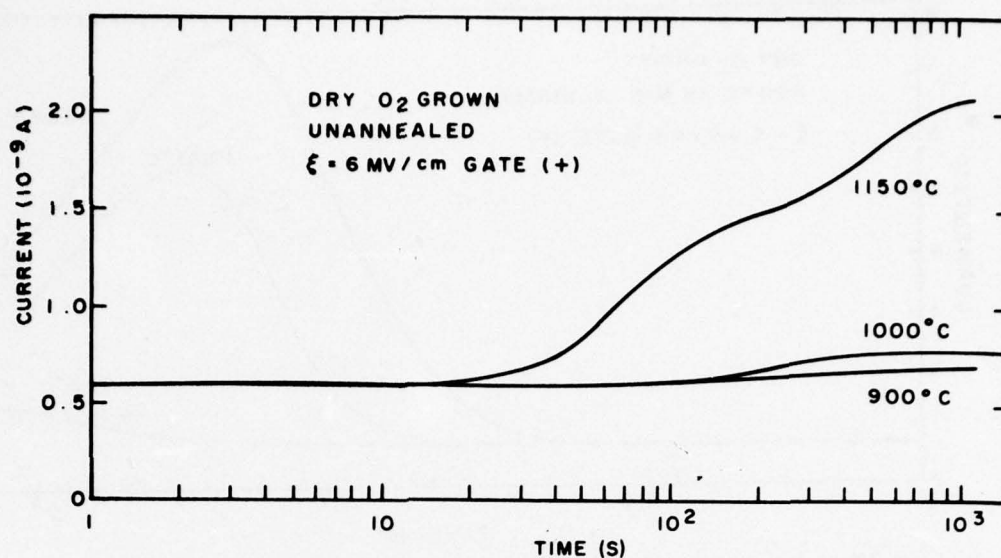


Figure 17. Time dependence of current during VUV irradiation for dry  $O_2$ -grown samples with different growth temperatures. Positive gate bias was used to produce an average field of 6 MV/cm in the oxide. The photon energy was 10.2 eV and  $SiO_2$  absorbed photon flux was  $4 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ .

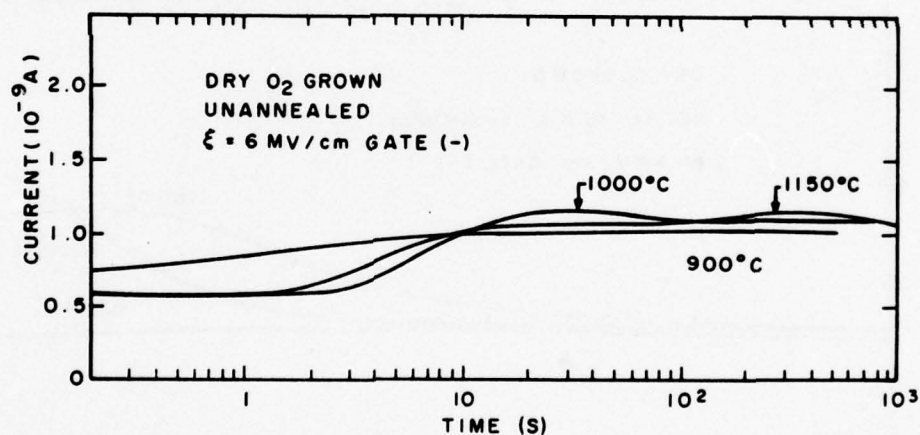


Figure 18. Time dependence of current during VUV irradiation for dry  $O_2$ -grown samples with different growth temperatures. Negative gate bias was used. Other conditions were the same as in figure 17.

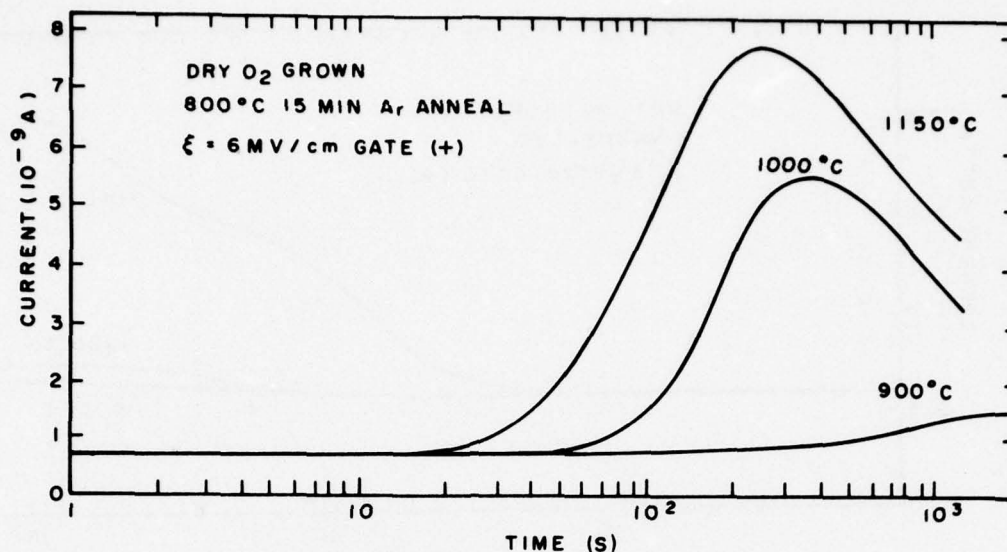


Figure 19. Time dependence of current during VUV irradiation for dry  $O_2$ -grown samples which were annealed in argon at  $800^\circ\text{C}$  for 15 min. Positive gate bias was used to produce an average oxide field of 6 MV/cm. The photon energy was 10.2 eV and the  $\text{SiO}_2$  absorbed photon flux was  $4 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ .

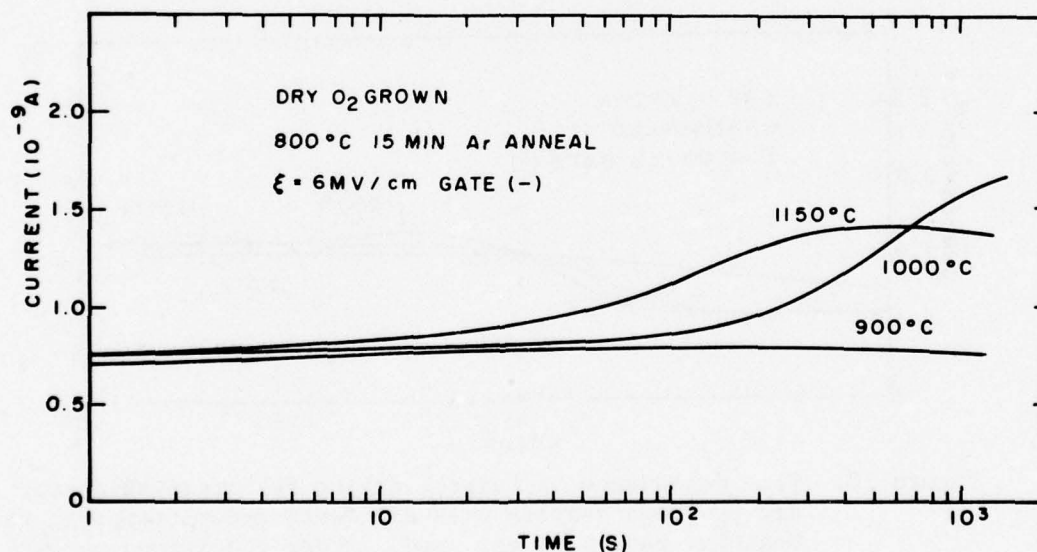


Figure 20. Time dependence of current during VUV irradiation for dry  $O_2$ -grown samples which were annealed in argon at  $800^\circ\text{C}$  for 15 min. Negative gate bias was used. Other conditions are the same as in figure 19.



in the  $\text{SiO}_2$  near the gate electrode. When sufficient space charge accumulates to raise the interface field close to 7 MV/cm, the current increases. The curves in figure 17 show the time dependence of total oxide current for samples with three different growth temperatures. It is apparent from these results that the smallest number of traps is obtained for the lowest growth temperature, 900°C, and the number increases with temperature. The curves in figure 18 depict the current-time characteristics of the unannealed samples under negative gate bias. In this case, holes generated in the shallow absorbing region near the gate are swept out to the gate. Some, however, are trapped in this region, and the accumulating space charge enhances the field at the gate until the current is enhanced by electron tunneling from the gate into the oxide. This experiment provides us with a method of estimating and comparing the number of hole traps effective in enhancing the field at the gate. A surprising fact is that for both the 900° and 1000°C samples the current enhancement is actually larger under negative gate bias than with positive bias. One might be tempted to suggest that in these samples the hole trapping is distributed throughout the oxide with the centroid lying somewhat closer to the gate for the 900° and 1000°C samples. However, that this is definitely not the case is readily proven. First, the trapping in the negative bias case must be almost entirely within 200 Å of the gate electrode because the absorption depth of the 10.2-eV light is only about 100 Å. Second, the capacitance-voltage flatband shifts for negative bias are seven to eight times smaller than for positive bias, as illustrated in figure 21, so we must conclude that the charge is very near the gate electrode following negative bias irradiation.

Charge trapped near the gate will have little effect on the current enhancement and flatband shift under positive bias, and charge is mostly near the Si-SiO<sub>2</sub> interface following positive bias irradiation. Using these facts, we can estimate the location of charge trapped near the gate following negative bias irradiation. The results of

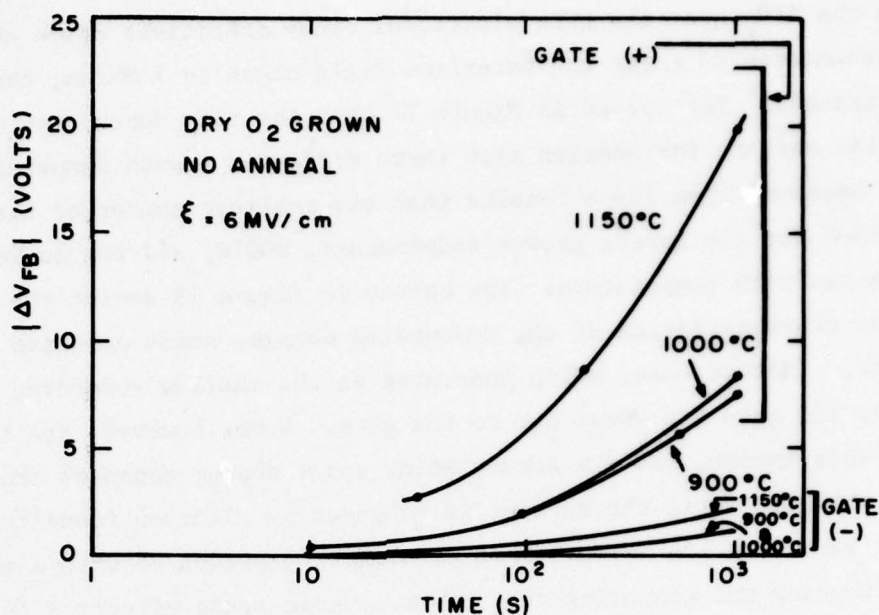


Figure 21. Flatband shift vs time during irradiation with positive and negative bias for un-annealed dry oxides.

figures 17 and 18 indicate that for the 900° and 1000°C samples, comparable amounts of charge are trapped near the silicon and aluminum. Since the  $|\Delta V_{FB}|$  for the two cases differs by a factor of  $\sim 7$ , the charge centroid for the negative bias case must be  $\sim 7$  times closer to the gate than for the positive bias case. This places the centroid within about 100 Å of the Al-SiO<sub>2</sub> interface. The above argument assumes that the trapped charge is as effective in producing current enhancement as it is in producing flatband shift. This is not true when charge is trapped extremely close to the interface (within  $\sim 30$  Å).<sup>25</sup>

<sup>25</sup>R. J. Powell, "Radiation and Charge Injection in Al<sub>2</sub>O<sub>3</sub> Using New Techniques," Final Report No. AFGL-TR-76-0017 for Air Force Geophysics Laboratory, January 1976.

Presented in figures 19 and 20 are curves which summarize the experimental results for VUV current enhancement experiments on the set of samples which was annealed in argon following oxidation. Focusing on figure 19, we first observe the greatly increased current enhancement compared with the unannealed samples in figure 17 (note scale differences between these figures). This result indicates that the argon anneal has markedly increased the number of oxide traps which are effective in producing current enhancement and flatband shifts. This statement is borne out by the flatband shift data shown in figure 22. The shifts here are in every case significantly larger than those of the unannealed oxides (fig. 21). The second observation is that the current begins to decrease for the 1000° and 1150°C oxides at about 250 to 300 s. As explained in section 2.3, this is due to a large increase in acceptor interface states. (Note that only acceptors are charged in positive bias current enhancement.)

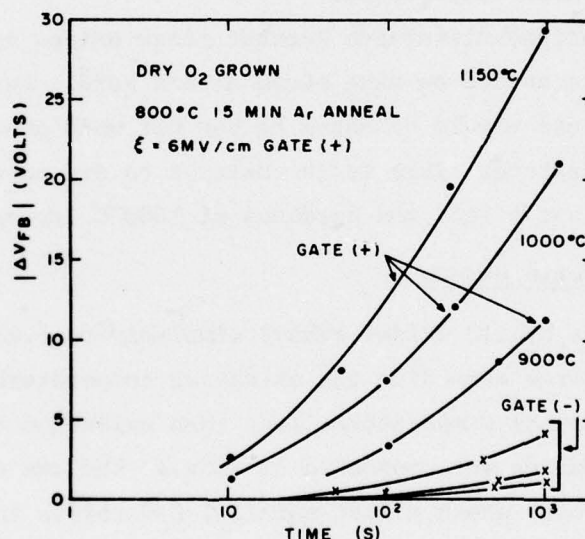


Figure 22. Flatband shift vs time during VUV irradiation with positive and negative gate bias for argon-annealed oxides.



A comparison of figures 20 and 18 shows that the trapping near the gate electrode has not been significantly increased by the argon anneal. These results suggest that the anneal does not appreciably change the basic trap structure of the oxide bulk and near the gate electrode, but does modify it markedly near the Si-SiO<sub>2</sub> interface.

#### 4.2.2 Pyrogenic Steam Oxides

In addition to the 900°, 1000°, and 1100°C annealed steam oxides, oxides were also annealed at 850°, 950°, and 1050°C for current-enhancement measurements. Figure 23 shows these results. It is interesting to note here that the minimum current enhancement occurs at 1000°C and the minimum flatband shift occurs at 900°C for high energy irradiation (see fig. 7) and VUV irradiation up to 500 s (fig. 24). It may be that acceptor interface states compensate the trapped holes for current enhancement even before the current starts rising. For hard oxides such as these, a higher applied field is needed to see the effects of hole traps first.

One important difference between steam oxides and dry oxides is that anneals are needed to make steam oxides hard. Furthermore, the anneal temperature should be equal to but not much greater than the oxidation temperature. This is in contrast to dry oxides where anneals below 800°C do not affect the hardness of 1000°C dry oxides at all.

#### 4.2.3 Hybrid Oxides

The hybrid oxides behave similarly to steam oxides for anneal temperatures exceeding the oxidation temperature. (We do not have data for anneal temperatures less than oxidation temperatures since all the oxides were annealed *in situ*.) The one exception is the 1150°C anneal which shows almost parallel C-V shifts indicating very little interface state generation. This is supported by the DDCV and HFCV shifts as shown in figure 25. All the other anneals show acceptor interface state generation as reflected in the reversal of the DDCV  $\Delta V_{FB}$ . Figure 26 shows the current-enhancement characteristic for these oxides, and figure 27 shows the  $\Delta V_{FB}$  vs t data.

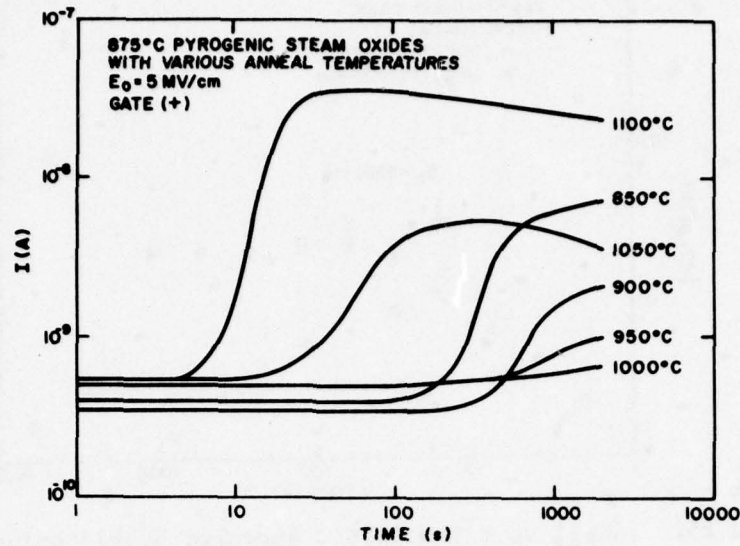


Figure 23. Time dependence of current during irradiation for pyrogenic steam oxides which were annealed at the temperatures shown. Positive gate bias of 5 MV/cm was used. Other conditions were the same as in figure 17.

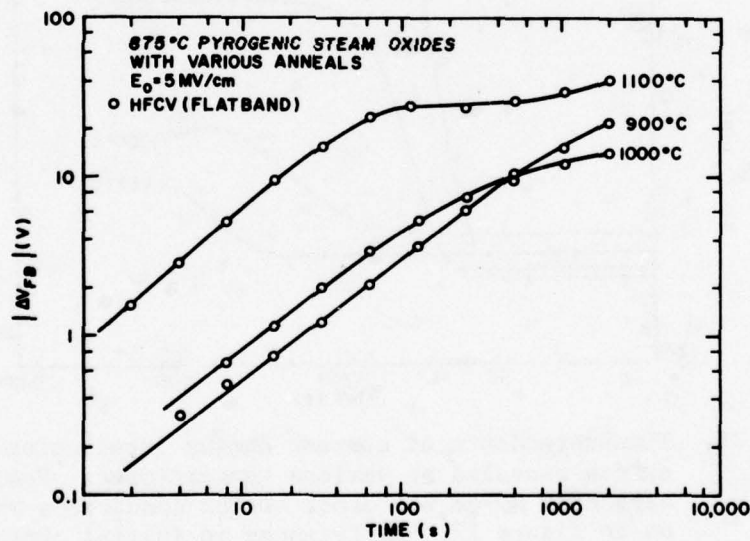


Figure 24.  $|\Delta V_{FB}|$  vs  $t$  for various anneals of pyrogenic steam oxide. Positive gate bias of 5 MV/cm was used.

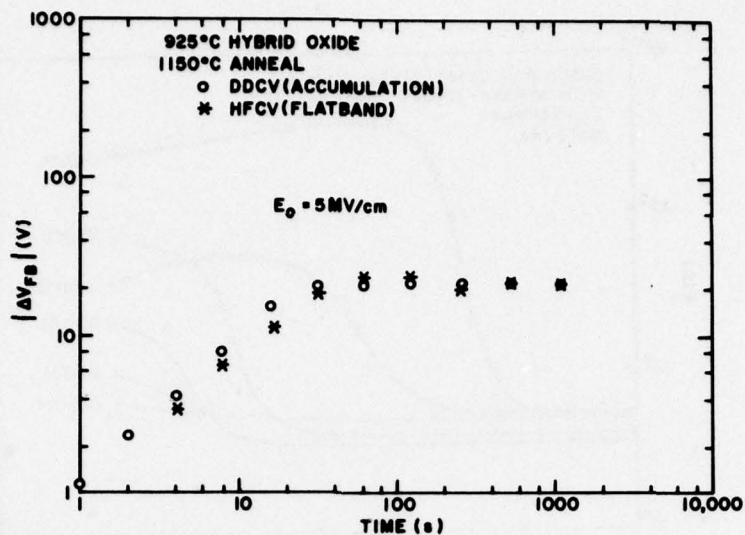


Figure 25.  $|\Delta V_{FB}|$  vs  $t$  for 1150°C annealed hybrid oxide illustrating little interface state generation.

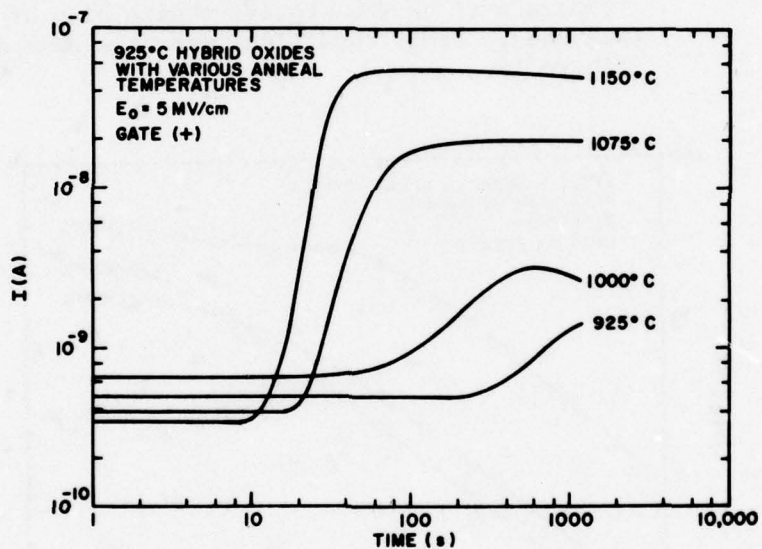


Figure 26. Time dependence of current during irradiation for hybrid oxides annealed at various temperatures. Positive gate bias of 5 MV/cm was used. Other conditions were the same as in figure 17. Differences in initial photocurrent due to varying thickness of semitransparent Al gate.



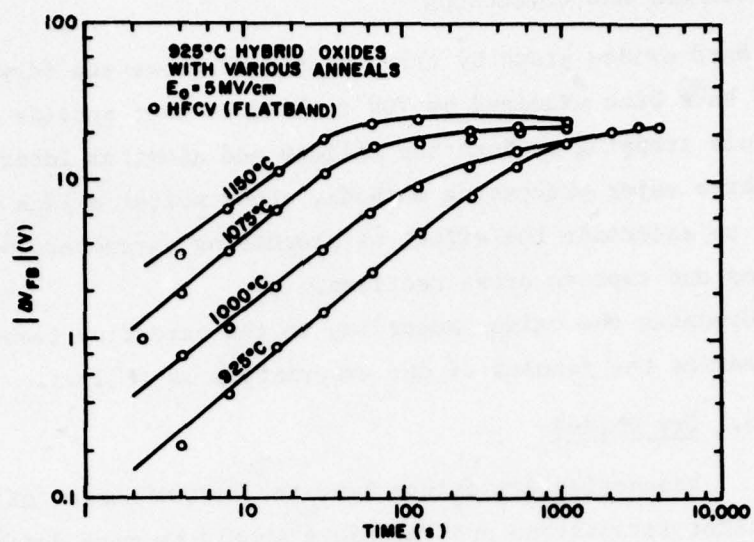


Figure 27.  $|\Delta V_{FB}|$  vs  $t$  data for hybrid oxides annealed at various temperatures. Positive gate bias of 5 MV/cm was used.

## 5. SUMMARY AND CONCLUSION

Hard oxides grown by three different processes (dry, wet, and hybrid) have been examined by VUV techniques that provide information about hole trapping at both the silicon and aluminum interface. Within these three major processing methods, other softer oxides were also studied to ascertain the effect of processing parameters on hole-trap densities and capture cross sections.

Grouping the oxides according to the oxidation technique, we can summarize the results of our experiments as follows.

### 5.1 Dry Oxides

Unannealed dry oxides have the lowest number of interface states after irradiation and therefore should be more desirable for radiation applications where parameters such as switching speed are important. As a group these oxides are dominated by a hole trap with  $S \sim 5 \times 10^{-14} \text{ cm}^2$  at 1 MV/cm. The DDCV measurements show no reversal in the  $\Delta V_{FB}$  vs  $t$  data so that the few interface states seen after irradiation are probably donors.

Current-enhancement measurements were made on both annealed and unannealed oxides under positive and negative bias. The unannealed oxides show no enhancement reversal for any of the growth temperatures indicating few acceptor interface states. The 900° and 1000°C oxides are very hard with little current enhancement even at  $E_o = 6 \text{ MV/cm}$ . The enhancement under negative bias is actually larger than under positive bias for the 900° and 1000°C oxide which shows that more charge is trapped at the aluminum interface than at the silicon interface for these samples.

Annealing these oxides in argon substantially increases not only the number of hole traps near the silicon interface but also the number of acceptor interface states. The density of the hole traps near the aluminum interface is not affected much by the argon anneal.

## 5.2 Steam Oxide

Pyrogenic steam oxides have many more interface states than dry oxides even in hard samples. Many or all of these interface states are acceptors. As a group these oxides show  $S \sim 5 \times 10^{-14} - 10^{-13}$  for  $E_o = 1$  MV/cm. The hardness of these oxides for high-energy irradiation ranges over an order of magnitude in  $\Delta V_{FB}$  depending upon anneal temperature. Since all capture cross sections appear to be the same, the wide variation in  $\Delta V_{FB}$  must be due to wide differences in hole trap and/or interface state densities. Current enhancement measurements show a very strong dependence on anneal temperature with 1000°C having the least enhancement and 850° and 1100°C the most. It is believed that the 900°C annealed oxide has the least number of hole traps and that the 1000°C oxide has less enhancement because of more acceptor interface states. The optimum anneal temperature for steam oxides is equal to or not much greater than the oxidation temperature.

## 5.3 Hybrid Oxides

In contrast to the other two processes, the hybrid oxides show  $S \sim 2 \times 10^{-13} \text{ cm}^2$  (at  $E_o = 1$  MV/cm) up to 4 times larger than the wet or dry oxide capture cross sections. This is the only group of oxides grown with HCl present during oxidation. It is suspected that the HCl modifies the  $\text{SiO}_2$  properties to the extent that the capture cross section is different. More than the other oxides the capture cross sections for the hybrid oxides overlap within the group. The main differences appear to be the hole trap and interface state density (of which many are acceptors).

The current-enhancement data for the hybrid oxides is similar to the wet oxide data. The enhancement increases with anneal temperature and has a minimum at the oxidation temperature. One anomaly among all the oxides is the 1150°C annealed hybrid oxide. It has a very large flatband voltage shift and current enhancement but very few interface states. All other hybrid oxides show substantial acceptor interface-state generation.



If we make the assumption that different hole traps have substantially different capture cross sections, then the wet and dry oxide data support the conclusion that the same trap is responsible for radiation charging in both oxides. This is somewhat surprising in view of the fact that the oxides are grown by completely different processes. However, it may be that the anneal of steam oxides in an inert ambient restructures the Si-SiO<sub>2</sub> interfacial region to be more like dry SiO<sub>2</sub>.

The field dependence of the capture cross section was explained in section 4 as resulting from Poole-Frenkel type lowering of the short range potential barrier surrounding a neutral trap. This could have favorable implications for radiation hardening if devices are not irradiated to saturation. If MOS transistors are fabricated with thin oxides, then not only will the oxide field be larger for a given supply voltage, but the thickness dependence of  $\Delta V_{FB}$  will make the device much harder.<sup>26,27</sup>

Because of the various limitations of the measurement technique described in section 3 it is not possible to measure  $S$  and  $N_T$  with any greater accuracy using this method. Ning has shown how these parameters can be measured more accurately if one can measure both the injected charge and the flatband shift to a high degree of accuracy.<sup>21</sup> Because of possible charge detrapping with changes in bias, it is not possible to measure  $\Delta V_{FB}$  more accurately using MOS capacitors. Ning has used MOS transistors to measure threshold-voltage shifts very accurately, presumably because the oxide field is unchanged throughout the measurement.<sup>21</sup> Unfortunately his technique relies on injected

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<sup>26</sup>G. F. Derbenwick and B. L. Gregory, *IEEE Trans. Nucl. Sci.* NS-22, 2151 (1975).

<sup>27</sup>G. W. Hughes, R. J. Powell, and M. H. Woods, *Appl. Phys. Lett.* 29, 377 (1976).

charge from the silicon interface as the probe. This places a limitation on the maximum trapping efficiency that can be measured ( $P_{co} \leq 0.1$ ). With VUV hole and electron excitation at the gate interface, this limitation is overcome since all charge arriving at the Si-SiO<sub>2</sub> interface is measured as a displacement current in the external circuit whether it is trapped or not. Using Ning's approach for measuring threshold-voltage shifts and exciting holes (or electrons) with 10.2-eV VUV photons, we should be able to measure  $S$  and  $N_T$  over a much wider range of cross sections and with much more accuracy than has been demonstrated at this time. This holds true for hole and electron capture cross sections.

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**APPENDIX**

## APPENDIX A. CALCULATION OF CAPTURE CROSS SECTION AND TRAP DENSITY

To calculate the capture cross section  $S$  and the trap density  $N_T$  for the various oxides, two different sets of data are needed. The initial flatband shift as a function of time is used to determine the product  $N_T S$  through the use of equation (21) from the main body of this report. This assumes  $\Delta V_{FB}$  is initially linear with  $t$ . This is true for most oxides, but there is one exception: the 925°C annealed hybrid oxide (see fig. A-1). Equation (21) was used for this case anyway, as a first approximation to  $N_T S$ . Figures A-1 through A-3 contain these data for all oxides measured at  $E_0 = 1$  MV/cm.

The final  $\Delta V_{FB}$  was determined from the DDCV and HFCV data as explained in section 3 of this report.  $\Delta V_{FB}$  is not a strong function of applied field as long as  $E_0$  is large enough to inhibit geminate recombination at the gate (see fig. 16 in the main body of the report). These measurements were only taken at  $E_0 = 5$  MV/cm. Fields of this magnitude as necessary to eliminate any reduction in hole generation rate due to charge build-up at the gate.<sup>A-1</sup> Figures 11 and 25 and figures A-4 through A-11 contain these data for all oxides measured at  $E_0 = 5$  MV/cm.

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<sup>A-1</sup>R. J. Powell, *J. Appl. Phys.* 46, 4557 (1975).



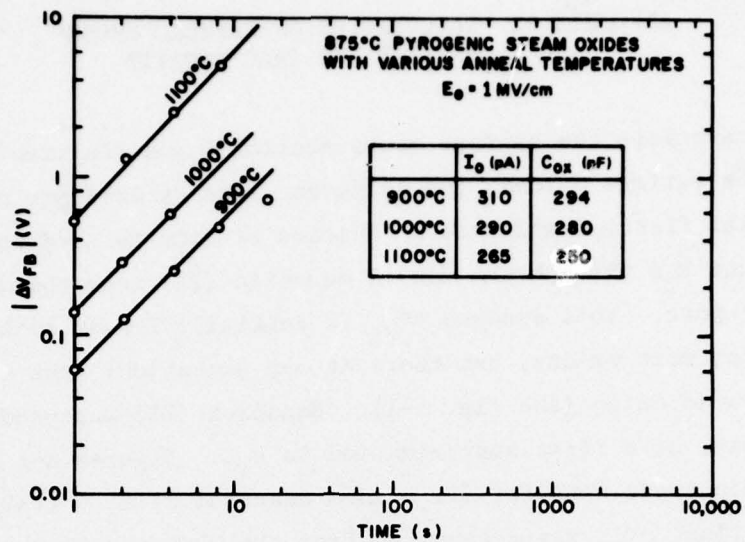


Figure A-1.  $|\Delta V_{FB}|$  vs time "early" data for pyrogenic steam oxides annealed at various temperatures.

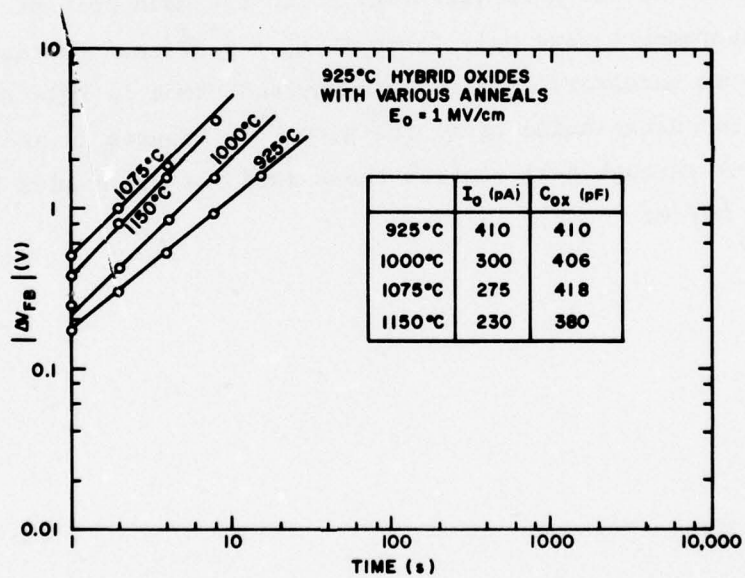


Figure A-2.  $|\Delta V_{FB}|$  vs time "early" data for hybrid oxides annealed at various temperatures.

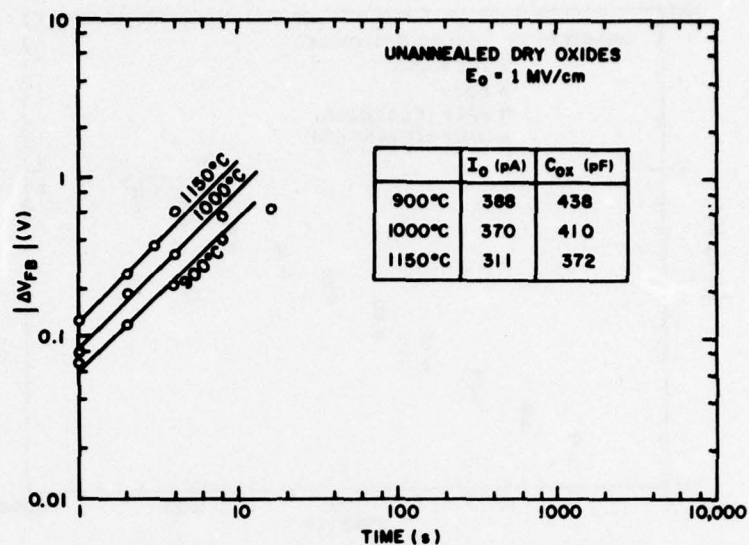


Figure A-3.  $|\Delta V_{FB}|$  vs time "early" data for unannealed dry oxides grown at various temperatures.

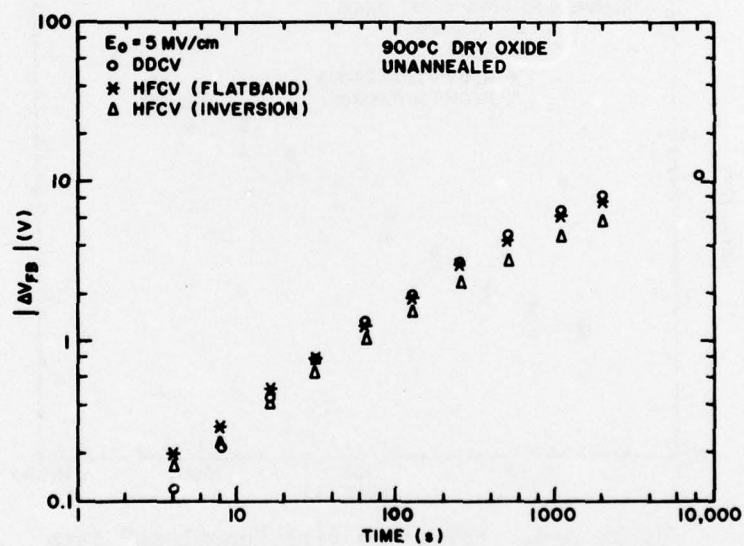


Figure A-4.  $|\Delta V_{FB}|$  vs time "complete" data for 900°C dry oxides.

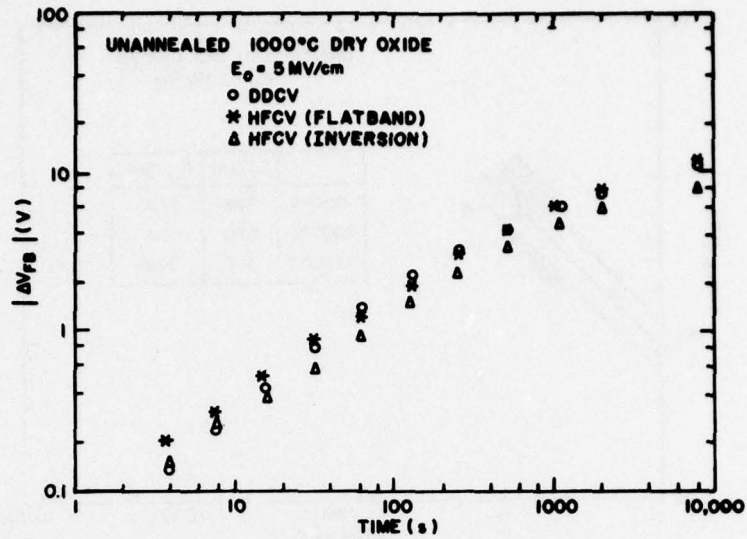


Figure A-5.  $|\Delta V_{FB}|$  vs time "complete" data for 1000°C dry oxides.

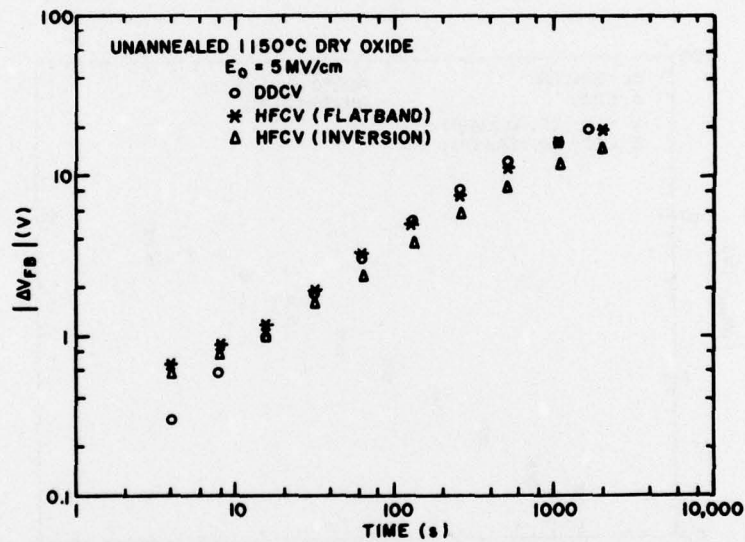


Figure A-6.  $|\Delta V_{FB}|$  vs time "complete" data for 1150°C dry oxides.



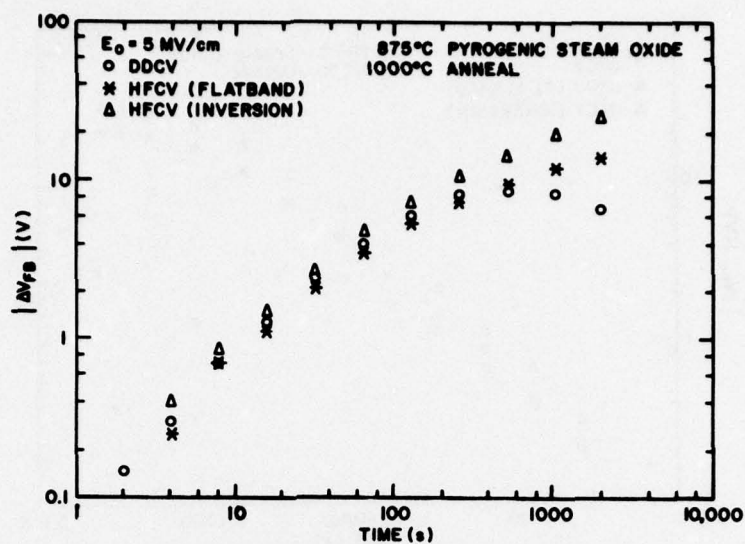


Figure A-7.  $|\Delta V_{FB}|$  vs time "complete" data for 1000°C annealed pyrogenic steam oxide.

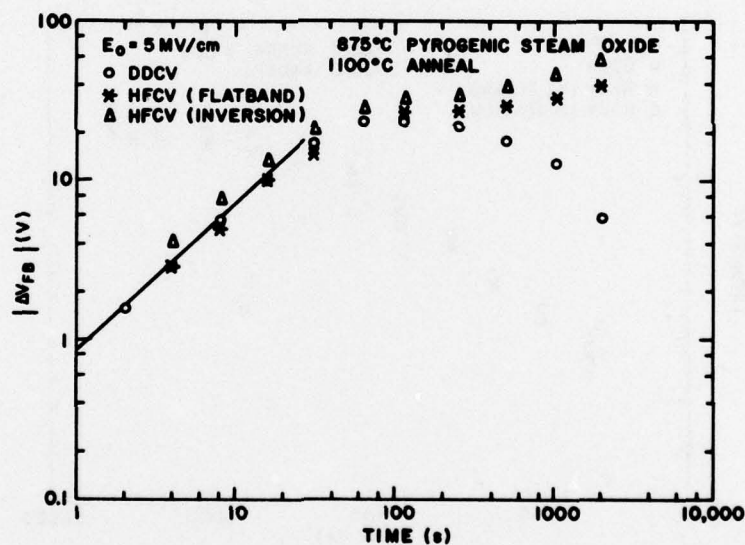


Figure A-8.  $|\Delta V_{FB}|$  vs time "complete" data for 1100°C annealed pyrogenic steam oxide.

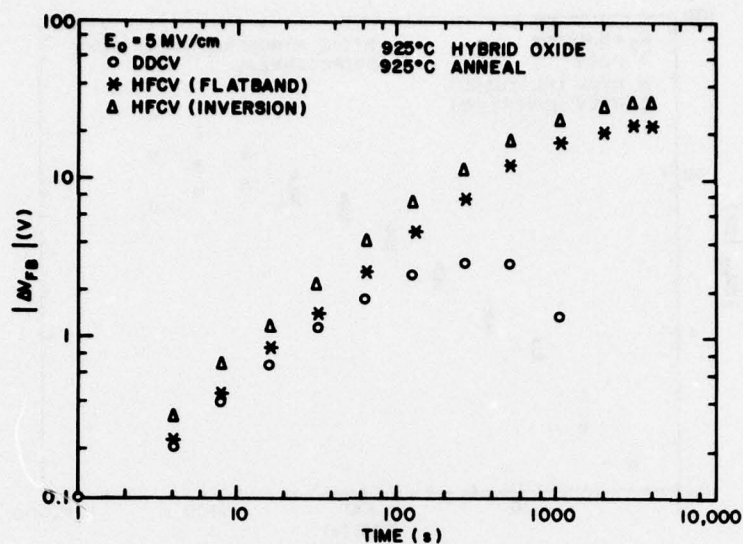


Figure A-9.  $|\Delta V_{FB}|$  vs time "complete" data for 925°C annealed hybrid oxide.

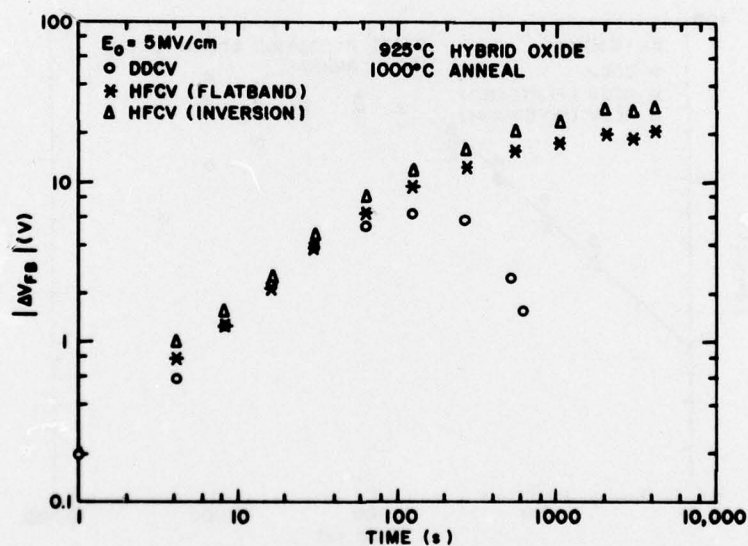


Figure A-10.  $|\Delta V_{FB}|$  vs time "complete" data for 1000°C annealed hybrid oxide.

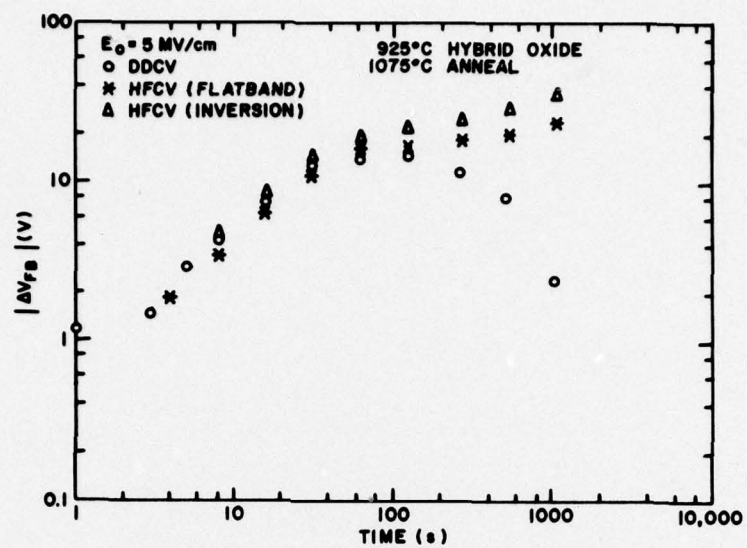


Figure A-11.  $|\Delta V_{FB}|$  vs time "complete" data for 1075°C annealed hybrid oxide.



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